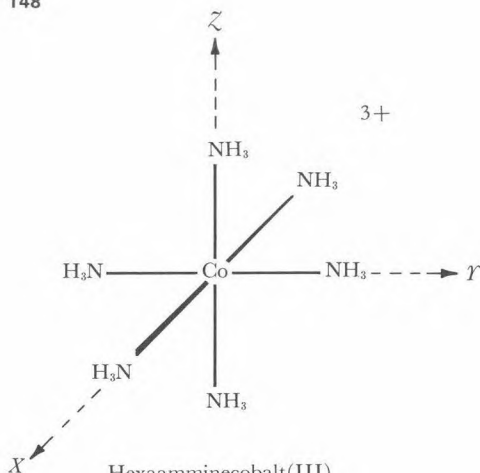
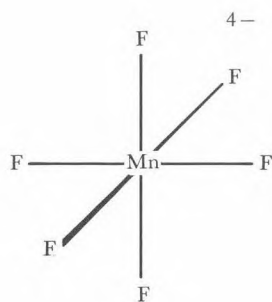


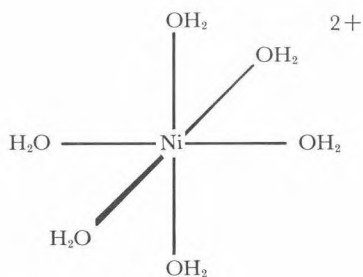
Transition-Metal Complexes



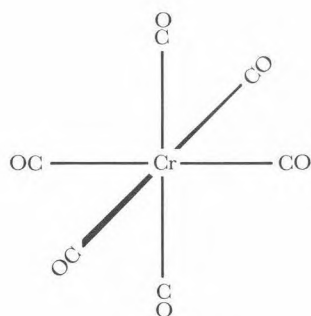
Hexaamminecobalt(III)
Color: yellow
Diamagnetic



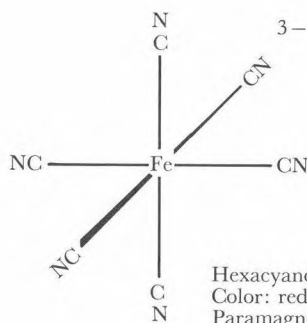
Hexafluoromanganate(II)
Color: pink
Paramagnetic (5 unpaired electrons)



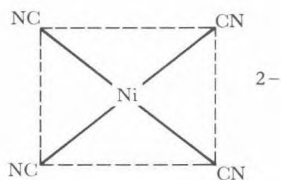
Hexaaquanickel(II)
Color: green
Paramagnetic (2 unpaired electrons)



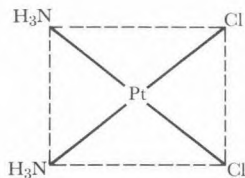
Hexacarbonylchromium(0)
Color: white
Diamagnetic



Hexacyanoferrate(III) or "ferricyanide"
Color: red
Paramagnetic (1 unpaired electron)

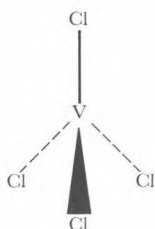


Tetracyanonickelate(II)
Color: yellow
Diamagnetic

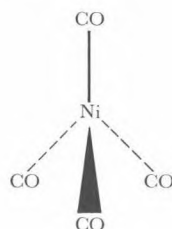


cis-Dichlorodiammineplatinum(II)
Color: yellow
Diamagnetic

Square planar

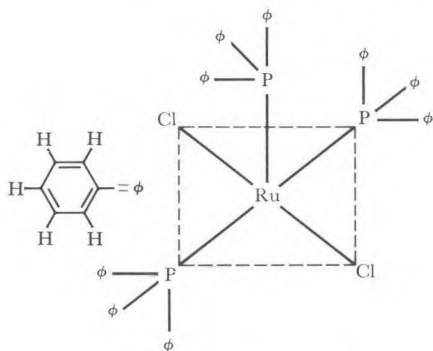


Tetrachlorovanadium(IV)
Color: red-brown
Paramagnetic (1 unpaired electron)

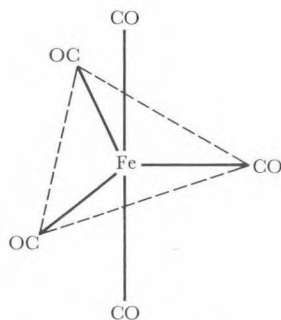


Tetracarbonylnickel(0)
Color: colorless
Diamagnetic

Tetrahedral



Square pyramidal
trans-Dichloro(tris)triphenyl-
phosphineruthenium(II)
Color: brown
Diamagnetic



Trigonal bipyramidal
Pentacarbonyliron(0)
Color: yellow
Diamagnetic

5-1

Several metal complexes, with systematic names, colors, and magnetic properties.

The transition metals (or *d*-electron elements) form a wide variety of compounds with interesting spectroscopic and magnetic properties. Many of these compounds, or complexes as they often are called, are catalysts in important industrial chemical processes. Furthermore, several transition-metal ions are necessary components of biochemical systems. The electronic structures of transition-metal complexes have been studied extensively in the past twenty years.

In discussing the structures of metal complexes it is convenient to use the term *coordination number*, which is defined as the number of atoms bonded directly to the central metal atom. The groups attached to the metal are called *ligands*. Each ligand has one or more donor atoms that bond to the metal. Emphasis has been on coordination numbers four and six, which are by far the most common among transition-metal complexes. Almost all of the six-coordinate complexes have an octahedral structure. Both square planar and tetrahedral geometries are prominent for four-coordinate complexes. A large number of complexes of metal ions with d^8 or d^9 electronic configurations have the square planar structure. For example, most of the Pd^{2+} ($4d^8$), Pt^{2+} ($5d^8$), and Au^{3+} ($5d^8$) complexes are square planar. Although tetrahedral complexes are formed by many metal ions of the first transition series (Sc–Zn), the occurrence of this structure in heavier ($4d$ and $5d$ series) metal ions is restricted mainly to d^0 and d^{10} configurations (e.g., MoO_4^{2-} , ReO_4^- , and HgI_4^{2-}).

Figure 5-1 shows examples of the most important geometries for coordination numbers four, five, and six. Recent research has shown the importance of the once rare square pyramidal and trigonal bipyramidal five-coordinate structures in the ground-state stereochemistry of many metal ions, particularly that of Ni^{2+} . Other lesser known coordination geometries, based on coordination numbers greater than six, now are receiving much attention.

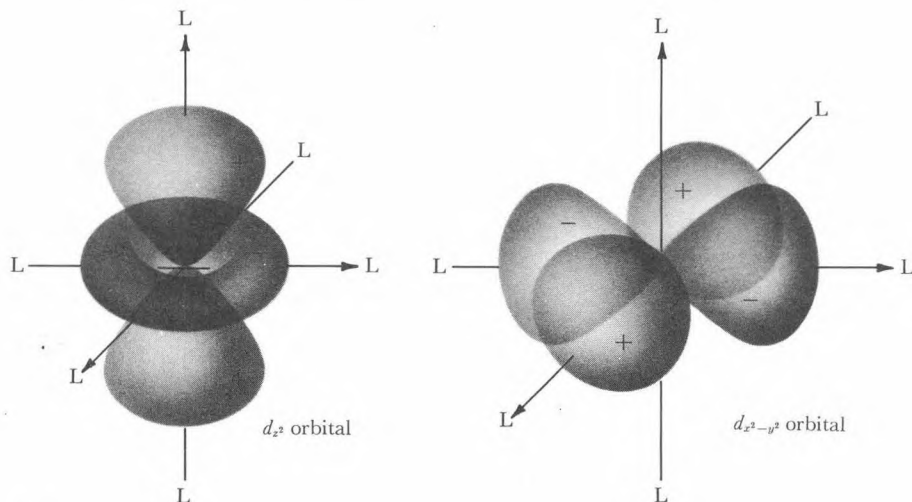
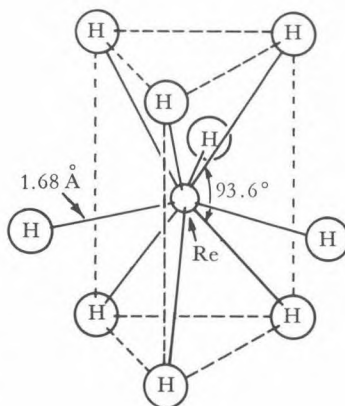
5-1 *d* ORBITALS IN BONDING

The maximum number of σ bonds that can be constructed from *s* and *p* valence orbitals is four. Thus four is the highest coordination number commonly encountered for central atoms with $2s$ and $2p$ valence orbitals. For example, in CH_4 the central carbon atom is “saturated” with four σ bonds. However, with a first-row transition metal as the central atom, there are five *d* valence orbitals in addition to the one *s* and three *p* valence orbitals. Specifically, a first-row transition metal atom has nine valence orbitals—five $3d$ orbitals, one $4s$ orbital, and three $4p$ orbitals.

If the central metal atom used all of its *d*, *s*, and *p* valence orbitals in σ bonding, a total of nine ligands could be attached. However, because of the large size of most ligands it is extremely difficult to achieve a coordination number of nine. Rhenium, a large third-row transition metal, and hydrogen,

5-2

The structure of the ReH_9^{2-} ion. There are six H atoms at the corners of a trigonal prism, and three more H atoms around the Re atom in a plane halfway between the triangular-end faces of the prism.

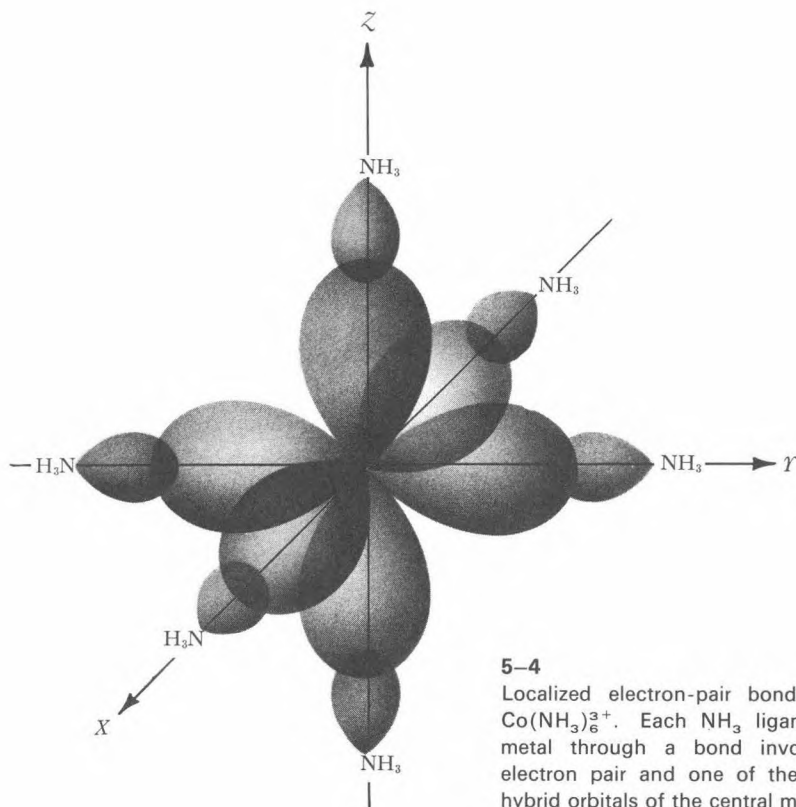


5-3

The spatial orientation of the d_{z^2} and $d_{x^2-y^2}$ orbitals in an octahedral complex. L represents a general ligand.

a small ligand, form the complex ReH_9^{2-} , which exhibits the coordination number of nine. The structure of this complex is shown in Figure 5-2.

Most first-row metal complexes have the coordination number six and an octahedral structure. Several octahedral complexes are shown in Figure 5-1. Six of the nine valence orbitals of the central atom are used in σ bonding in an octahedral structure, namely the $3d_{x^2-y^2}$, $3d_{z^2}$, $4p_x$, $4p_y$, $4p_z$, and $4s$. Notice that the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are directed toward the ligands, as shown in Figure 5-3. In localized molecular-orbital language six d^2sp^3 hybrid orbitals



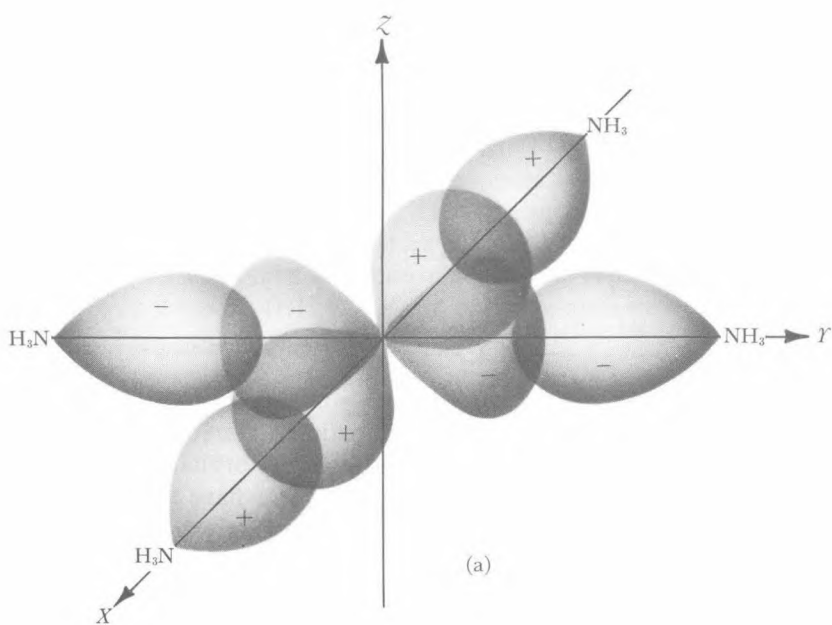
5-4

Localized electron-pair bonding representation of $\text{Co}(\text{NH}_3)_6^{3+}$. Each NH_3 ligand is attached to the metal through a bond involving the NH_3 lone electron pair and one of the six equivalent d^2sp^3 hybrid orbitals of the central metal ion.

are used to attach the six ligands, as shown in Figure 5-4. However, the localized molecular orbital theory is inadequate for explaining the colors and magnetic properties of transition-metal complexes. The model of greatest utility in discussing the properties of metal complexes is based on delocalized molecular orbital theory. Because the model emphasizes the interaction of the d valence orbitals of the metal atoms with appropriate ligand orbitals, it is called *ligand field theory*.

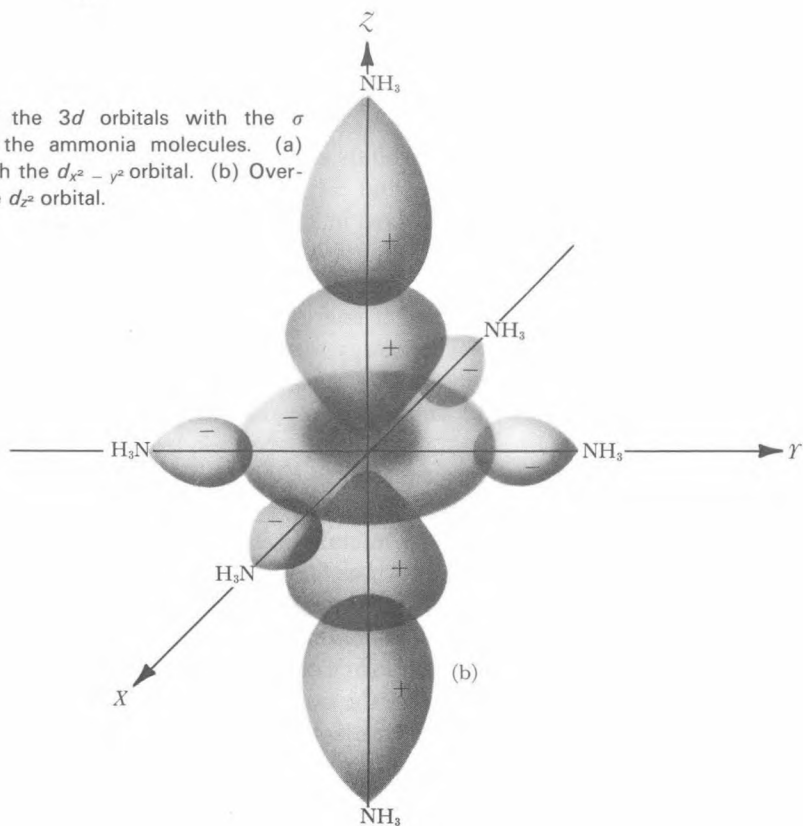
5-2 LIGAND FIELD THEORY FOR OCTAHEDRAL COMPLEXES

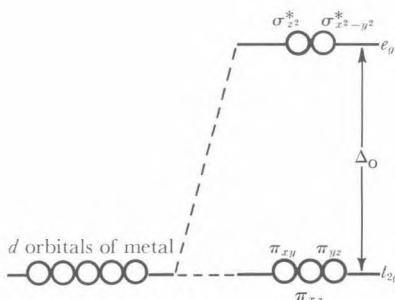
Consider the five $3d$ orbitals in a metal complex such as $\text{Co}(\text{NH}_3)_6^{3+}$. To describe the bonding we choose a coordinate system in which the X , Y , and Z axes go through the nitrogen nuclei. The $\text{Co } 3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals overlap the approximately sp^3 lone-pair orbitals of the six NH_3 groups, as shown in Figure 5-5. As we did for diatomic molecules, we combine the metal and ligand



5-5

Overlap of the 3d orbitals with the σ orbitals of the ammonia molecules. (a) Overlap with the $d_{x^2 - y^2}$ orbital. (b) Overlap with the d_{z^2} orbital.





5-6

Ligand-field splitting in an octahedral complex.

orbitals in appropriate linear combinations, thereby forming two bonding orbitals, $\sigma_{z^2}^b$ and $\sigma_{x^2-y^2}^b$, and two antibonding orbitals, $\sigma_{z^2}^*$ and $\sigma_{x^2-y^2}^*$. The antibonding molecular orbitals $\sigma_{z^2}^*$ and $\sigma_{x^2-y^2}^*$ have much more metal than ligand character, and often are referred to simply as the “metal” $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals.

To construct the σ molecular orbitals we did not use three of the five $3d$ valence orbitals in the cobalt atom, specifically, the $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$. These orbitals are directed between the ligands and are projected into “free” space. Therefore these d orbitals are not situated properly for σ bonding in $\text{Co}(\text{NH}_3)_6^{3+}$. Consequently the originally degenerate five $3d$ valence orbitals, in which the electrons have equal energy in the free atom, divide into two sets in an octahedral complex. The $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are involved in the σ molecular-orbital system, whereas the $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$ orbitals are nonbonding or, with appropriate ligands, may be involved in a π molecular-orbital system.

The two orbital sets, $\sigma_{x^2-y^2}^*$, $\sigma_{z^2}^*$ (or $3d_{x^2-y^2}$, $3d_{z^2}$) and π_{xz} , π_{yz} , π_{xy} (or $3d_{xz}$, $3d_{yz}$, $3d_{xy}$) are called *ligand-field levels*. As shown in Figure 5-6, the $\sigma_{x^2-y^2}^*$ and $\sigma_{z^2}^*$ orbitals always have higher energy than the π_{xz} , π_{yz} , and π_{xy} orbitals in an octahedral complex. The energy separation of the $\sigma^*(d)$ and $\pi(d)$ levels is called the *octahedral ligand-field splitting* and is abbreviated Δ_o . The higher two orbitals commonly are denoted by e_g , and the lower three orbitals are denoted by t_{2g} .

The twelve electrons furnished by the six NH_3 ligands occupy six bonding molecular orbitals constructed from the NH_3 lone-pair orbitals and the $3d_{z^2}$, $3d_{x^2-y^2}$, $4s$, $4p_x$, $4p_y$, and $4p_z$ metal orbitals. The bonding combinations are very stable and will not concern us further. They are analogous to the six d^2sp^3 bonding orbitals in the localized molecular-orbital description. Also, we will not need to consider the antibonding orbitals derived from the $4s$ and $4p$ metal atomic orbitals, because these orbitals are very energetic. The important orbitals for our discussion comprise the two ligand-field levels, t_{2g} and e_g , shown in Figure 5-6. Because the valence electronic structure of Co^{3+} is $3d^6$, there are six valence electrons available to place in the t_{2g} and e_g levels. There are

two possibilities, depending on the value of Δ_o . In $\text{Co}(\text{NH}_3)_6^{3+}$, Δ_o is sufficiently large to allow all six d electrons to fill the t_{2g} level, thereby giving the ground-state electronic structure $(t_{2g})^6$, with all electrons paired. However, if Δ_o is smaller than the required electron-pairing energy, as happens in the Co^{3+} complex CoF_6^{3-} , the d electrons occupy the t_{2g} and e_g levels to give the maximum number of unpaired spins. The ground-state structure of CoF_6^{3-} is $(t_{2g})^4(e_g)^2$, with four unpaired electrons. Because of the difference in the number of unpaired electron spins in the two complexes, $\text{Co}(\text{NH}_3)_6^{3+}$ is said to be *low-spin*, whereas CoF_6^{3-} is referred to as a *high-spin complex*.

Table 5-1. Unpaired electrons in uncomplexed metal ions

| Ion | Number of d electrons | Number of unpaired d electrons |
|------------------|-------------------------|----------------------------------|
| Sc^{3+} | 0 | 0 |
| Ti^{3+} | 1 | 1 |
| V^{2+} | 3 | 3 |
| V^{3+} | 2 | 2 |
| Cr^{2+} | 4 | 4 |
| Cr^{3+} | 3 | 3 |
| Mn^{2+} | 5 | 5 |
| Fe^{2+} | 6 | 4 |
| Fe^{3+} | 5 | 5 |
| Co^{2+} | 7 | 3 |
| Co^{3+} | 6 | 4 |
| Ni^{2+} | 8 | 2 |
| Cu^{2+} | 9 | 1 |
| Zn^{2+} | 10 | 0 |

Next we will consider the ground-state electronic configurations of octahedral complexes that contain central metal ions other than Co^{3+} . Table 5-1 gives the number of unpaired d electrons in first-row dipositive and tripositive transition-metal ions that commonly are observed in octahedral coordination complexes. In each case the d^n configuration and the number of unpaired d electrons for the uncomplexed metal ion are given for reference. Referring to Figure 5-6 we see that metal ions with one, two, and three valence electrons will have the respective ground-state configurations $(t_{2g})^1$, $(t_{2g})^2$, and $(t_{2g})^3$. There are two possible ground-state configurations for the metal d^4 configuration, depending on the value of Δ_o in the complex. If Δ_o is less than the energy required to pair two d electrons in the t_{2g} level, the fourth electron will go into the e_g level, thereby giving the high-spin configuration $(t_{2g})^3(e_g)^1$, with four unpaired electrons. Ligands that form high-spin complexes are called *weak-field ligands*.

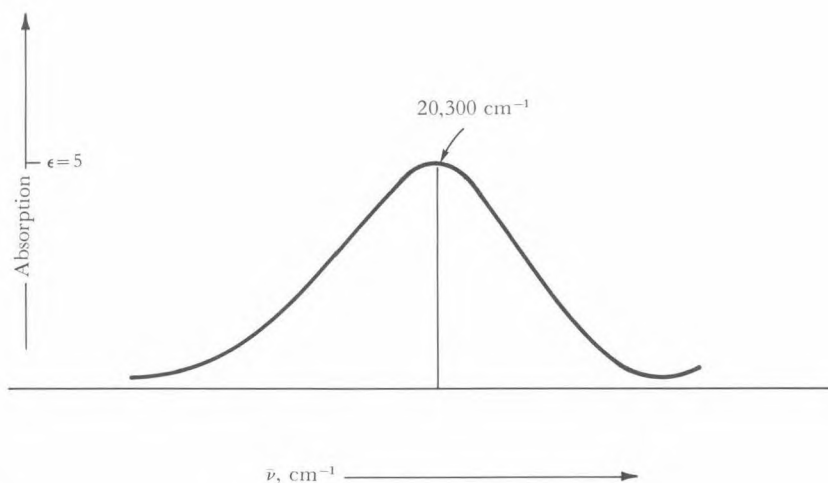
However, if Δ_o is larger than the required electron-pairing energy, the fourth electron will go into the lower-energy t_{2g} level and pair with one of the three electrons already present in that level. In this situation the ground state of the complex is the low-spin configuration $(t_{2g})^4$, with only two unpaired electrons. Ligands that cause splittings large enough to allow electrons to occupy preferentially the more stable t_{2g} level to give low-spin complexes are called *strong-field ligands*.

In filling the t_{2g} and e_g energy levels the electronic configurations d^5 , d^6 , and d^7 , as well as d^4 , can exhibit either a high-spin or a low-spin ground state, depending on the value of Δ_o in the complex. For a given d^n configuration the paramagnetism of a high-spin complex is larger than that of a low-spin complex. Examples of octahedral complexes with the possible $(t_{2g})^x(e_g)^y$ configurations are given in Table 5-2.

Table 5-2. Electronic configurations of octahedral complexes

| Electronic configuration of the metal ion | Electronic structure of the complex | Number of unpaired electrons | Example |
|---|-------------------------------------|------------------------------|--|
| $3d^1$ | $(t_{2g})^1$ | 1 | $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ |
| $3d^2$ | $(t_{2g})^2$ | 2 | $\text{V}(\text{H}_2\text{O})_6^{3+}$ |
| $3d^3$ | $(t_{2g})^3$ | 3 | $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ |
| $3d^4$ | Low-spin; $(t_{2g})^4$ | 2 | $\text{Mn}(\text{CN})_6^{3-}$ |
| | High-spin; $(t_{2g})^3(e_g)^1$ | 4 | $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ |
| $3d^5$ | Low-spin; $(t_{2g})^5$ | 1 | $\text{Fe}(\text{CN})_6^{3-}$ |
| | High-spin; $(t_{2g})^3(e_g)^2$ | 5 | $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ |
| $3d^6$ | Low-spin; $(t_{2g})^6$ | 0 | $\text{Co}(\text{NH}_3)_6^{3+}$ |
| | High-spin; $(t_{2g})^4(e_g)^2$ | 4 | CoF_6^{3-} |
| $3d^7$ | Low-spin; $(t_{2g})^6(e_g)^1$ | 1 | $\text{Co}(\text{NO}_2)_6^{4-}$ |
| | High-spin; $(t_{2g})^5(e_g)^2$ | 3 | $\text{Co}(\text{H}_2\text{O})_6^{2+}$ |
| $3d^8$ | $(t_{2g})^6(e_g)^2$ | 2 | $\text{Ni}(\text{NH}_3)_6^{2+}$ |
| $3d^9$ | $(t_{2g})^6(e_g)^3$ | 1 | $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ |

The first-row transition-metal ions that form the largest number of stable octahedral complexes are Cr^{3+} (d^3), Ni^{2+} (d^8), and Co^{3+} (d^6). The +3 central-ion charge for chromium and cobalt apparently is large enough for strong σ bonding, but not so large that the ligands would be oxidized and the complex destroyed. Furthermore, the orbital configurations $(t_{2g})^3$ and $(t_{2g})^6$ take maximum advantage of the low-energy t_{2g} level; $(t_{2g})^3$ corresponds to a half-filled t_{2g} shell, which requires no electron-pairing energy, and $(t_{2g})^6$ is the closed-shell structure. The $(t_{2g})^6(e_g)^2$ configuration of octahedral Ni^{2+} complexes features a filled t_{2g} and a half-filled e_g level, therefore complexes that exhibit relatively small Δ_o values are quite stable.



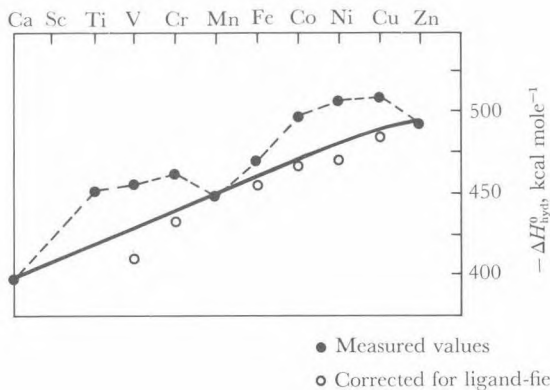
5-7

The absorption spectrum of $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ in the visible region.

d-d Transitions and light absorption

An electron in the t_{2g} level of an octahedral complex can absorb a light photon in the near-infrared, visible, or ultraviolet region and make a transition to an unoccupied orbital in the more energetic e_g level. Electron excitations of this type are called *d-d transitions*. Although *d-d* transitions generally give rise to weak absorption bands, they are responsible for the characteristic colors of many transition-metal complexes. An example is the red-violet Ti^{3+} complex, $\text{Ti}(\text{H}_2\text{O})_6^{3+}$, whose ground state is $(t_{2g})^1$. Excitation of the electron from the t_{2g} orbital to the e_g orbital occurs with light absorption in the vicinity of 5000 \AA ($20,000 \text{ cm}^{-1}$). Figure 5-7 shows that maximum absorption occurs at 4930 \AA ($20,300 \text{ cm}^{-1}$), with a molar extinction coefficient (ϵ) of 5. The value of the octahedral ligand-field splitting, Δ_o , usually is expressed in wave numbers; thus we say that for $\text{Ti}(\text{H}_2\text{O})_6^{3+}$, $\Delta_o = 20,300 \text{ cm}^{-1}$.

The colors of many other transition metal complexes are due to *d-d* transitions. The number of absorption bands depends on the molecular geometry of the complex and the d^n configuration of the central metal atom. The intensities of the *d-d* bands also vary with geometry. The absorption bands in octahedral complexes such as $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ are weak (ϵ range of 1–500) because *d-d* transitions of the type $t_{2g} \rightarrow e_g$ are orbitally forbidden. However, certain of the *d-d* transitions in tetrahedral complexes are fully allowed and can lead to fairly strong absorption (ϵ range of 200–5000). Thus, in many cases, the study of the electronic spectra of metal complexes is a powerful tool for determining molecular geometries.

**5-8**

Measured and ligand-field corrected values of heats of hydration of dipositive transition-metal ions. The heat of hydration is a measure of the $M-OH_2$ bond strength.

A special case of interest is the high-spin d^5 configuration, exhibited by the octahedral complex $Mn(H_2O)_6^{2+}$. The high-spin ground state for the five $3d$ electrons in $Mn(H_2O)_6^{2+}$ is $(t_{2g})^3(e_g)^2$, with five unpaired electrons. All $d-d$ transitions from this ground state are spin-forbidden (the transitions of lowest energy are to excited states with three unpaired electrons). The color of the Mn^{2+} ion in aqueous solution is very pale pink. The color results from the extremely low intensities (ϵ values of approximately 0.01) of the spin-forbidden $d-d$ absorption bands of $Mn(H_2O)_6^{2+}$, which lie in the visible region. (Weak absorption bands arising from electronic transitions that are “forbidden” according to orbital- or spin-selection rules were discussed first in Section 4-8.)

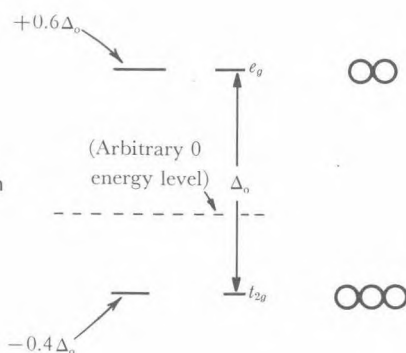
Heats of hydration of hexaquo complexes

A direct experimental indication of the special stability of certain d^n configurations in an octahedral ligand field is provided by the observed heats of hydration of dipositive transition-metal ions, as shown in Figure 5-8. If ionic size (thus the charge density on the central metal ion) were the only factor affecting bond energy, the curve would be approximately a straight line, thereby corresponding to a steady increase in bond energy from Ca^{2+} to Zn^{2+} as the ionic radii decrease. The double-humped curve indicates that, except for d^5 Mn^{2+} , the relative stabilization afforded by placing electrons preferentially in the t_{2g} level must make a substantial contribution to the hydration energy. As shown in Figure 5-9, each electron in the t_{2g} level will represent $0.4\Delta_o$ lower energy than the reference zero of energy, whereas each electron in the e_g level will be $0.6\Delta_o$ higher.

The relative ligand-field stabilization energies (LFSE) of the high-spin $M(H_2O)_6^{2+}$ complexes are given in Table 5-3. Ions such as Ti^{2+} , V^{2+} , Co^{2+} , and Ni^{2+} have large LFSE values and correspondingly large negative heats of hydration. After adjusting for LFSE, using Δ_o values derived from $d-d$

5-9

Relative energies of the t_{2g} and e_g orbitals in an octahedral ligand field.



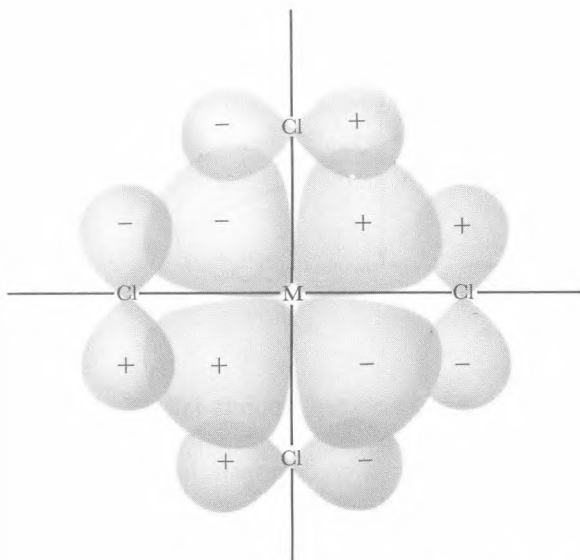
absorption spectra of the $M(H_2O)_6^{2+}$ complexes, the “corrected” points fall approximately on the $Ca^{2+}-Zn^{2+}$ line (Figure 5-8). The close correlation between data on heats of hydration and $d-d$ spectral information demonstrates the power of the ligand field theory.

Table 5-3. Ligand-field stabilization energies of $M(H_2O)_6^{2+}$ complexes

| M | Number of d electrons | | Stabilization energy (Δ_o units) |
|-----------|--------------------------|-----------------------|--|
| | Lower level (t_{2g}) | Upper level (e_g) | |
| Ca^{2+} | 0 | 0 | 0 |
| Ti^{2+} | 2 | 0 | 0.8 |
| V^{2+} | 3 | 0 | 1.2 |
| Cr^{2+} | 3 | 1 | 0.6 |
| Mn^{2+} | 3 | 2 | 0 |
| Fe^{2+} | 4 | 2 | 0.4 |
| Co^{2+} | 5 | 2 | 0.8 |
| Ni^{2+} | 6 | 2 | 1.2 |
| Cu^{2+} | 6 | 3 | 0.6 |
| Zn^{2+} | 6 | 4 | 0 |

π Bonding in metal complexes

The metal d_{xz} , d_{yz} , and d_{xy} valence orbitals may be used for π bonding to certain types of ligands in octahedral complexes. For example, consider a complex containing six chloride ligands. Each of the metal $d(\pi)$ orbitals overlaps with four ligand $3p(\pi)$ orbitals, as shown in Figure 5-10. In the bonding orbital some electronic charge from the chloride ions is transferred to the metal atom.



5-10

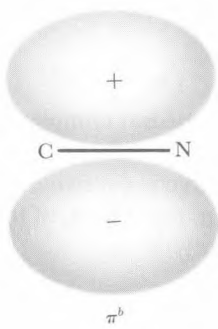
Overlap of a metal $d(\pi)$ orbital with four ligand $p(\pi)$ orbitals.

We call this *ligand-to-metal* ($L \rightarrow M$) π bonding. The π orbitals of the metal are destabilized in the process and become antibonding.

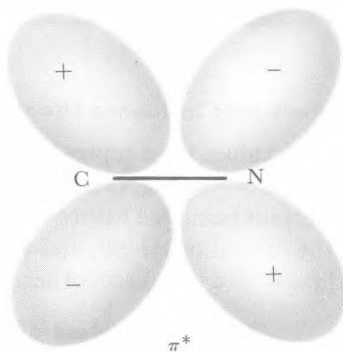
If the complex contains a diatomic ligand such as CN^- , two types of π bonding are possible. The occupied π^b ligand orbitals can enter into ($L \rightarrow M$) π bonding with the metal $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$ orbitals. However, electrons in the metal t_{2g} level also can be delocalized into the available ligand π^* (CN^-) orbitals, thereby preventing the accumulation of excess negative charge on the metal. This type of bonding removes electron density from the metal and is called *metal-to-ligand* ($M \rightarrow L$) π bonding. It also commonly is called *back donation* or *back bonding*. Back donation stabilizes the t_{2g} level and makes it less antibonding. ($L \rightarrow M$) π bonding is common when the central metal ion has a large positive charge and empty t_{2g} orbitals. ($M \rightarrow L$) π bonding is common when the central metal has low ionic charge and filled t_{2g} orbitals. Both types of π bonding between a $d(\pi)$ orbital and CN^- are shown in Figure 5-11.

5-11►

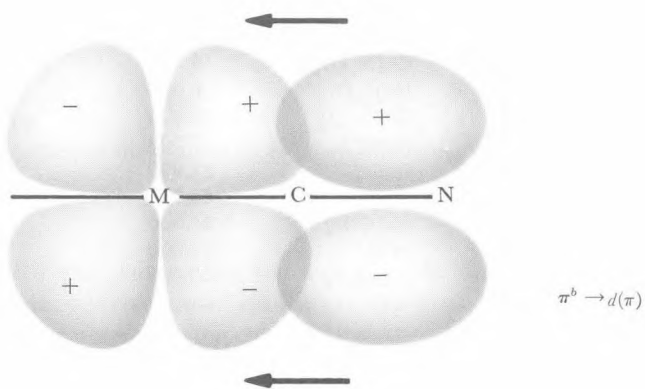
Two types of π bonding in metal complexes with a cyanide ion. (a) In the CN^- ion the bonding π^b molecular orbital contains an electron pair and the antibonding π^* orbital (b) is empty. (c) The metal orbitals of the t_{2g} type are more stable in the presence of simple σ -bonding ligands because the t_{2g} orbitals do not concentrate their electrons in the directions of the ligands. But if the ligand has filled π orbitals, then these orbitals interact with the metal t_{2g} orbitals and make them less stable. The splitting constant Δ_o decreases. (d) If the metal has filled t_{2g} orbitals that interact with the empty antibonding π ligand orbitals, then the metal electrons are delocalized, the energy of the orbitals decreases, and the splitting energy, Δ_o , increases. This last effect predominates in most CN^- complexes, thereby producing a large ligand-field splitting.



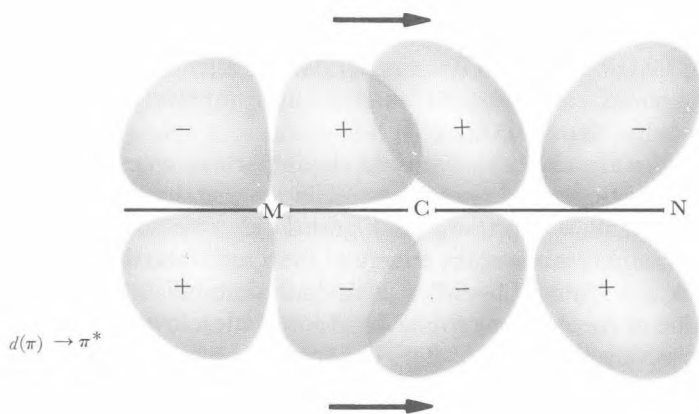
(a)



(b)



(c)



(d)

Factors that influence the value of Δ_o

The Δ_o values for a representative selection of octahedral complexes are given in Table 5-4. The value of Δ_o depends on a number of variables, the most important being the nature of the ligand, the ionic charge (or oxidation number) of the central metal ion, and the principal quantum number, n , of the d valence orbitals. We will discuss these variables individually.

Table 5-4. Values of Δ_o for representative octahedral metal complexes

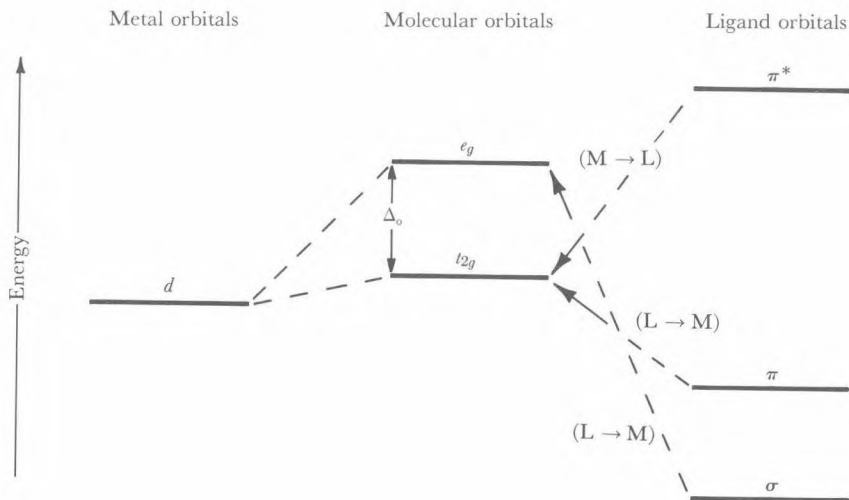
| Octahedral complexes | Δ_o, cm^{-1} | Octahedral complexes | Δ_o, cm^{-1} |
|--|----------------------------|--|----------------------------|
| TiF_6^{3-} | 17,000 | $\text{Co}(\text{NH}_3)_6^{3+}$ | 22,900 |
| $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ | 20,300 | $\text{Co}(\text{CN})_6^{3-}$ | 34,500 |
| $\text{V}(\text{H}_2\text{O})_6^{3+}$ | 17,850 | $\text{Co}(\text{H}_2\text{O})_6^{2+}$ | 9,300 |
| $\text{V}(\text{H}_2\text{O})_6^{2+}$ | 12,400 | $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ | 8,500 |
| $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ | 17,400 | $\text{Ni}(\text{NH}_3)_6^{2+}$ | 10,800 |
| $\text{Cr}(\text{NH}_3)_6^{3+}$ | 21,600 | RhBr_6^{3-} | 21,600 |
| $\text{Cr}(\text{CN})_6^{3-}$ | 26,600 | RhCl_6^{3-} | 22,800 |
| $\text{Cr}(\text{CO})_6$ | 32,200 | $\text{Rh}(\text{NH}_3)_6^{3+}$ | 34,100 |
| $\text{Fe}(\text{CN})_6^{3-}$ | 35,000 | $\text{Rh}(\text{CN})_6^{3-}$ | 44,000 |
| $\text{Fe}(\text{CN})_6^{4-}$ | 33,800 | IrCl_6^{3-} | 27,600 |
| $\text{Co}(\text{H}_2\text{O})_6^{3+}$ | 18,200 | $\text{Ir}(\text{NH}_3)_6^{3+}$ | 40,000 |

Nature of the ligand. The ordering of ligands in terms of their ability to split the e_g and t_{2g} molecular orbitals is known as the *spectrochemical series*. The order of ligand-field splitting of some important ligands is



Octahedral complexes containing ligands such as CN^- and CO , which are at the strong-field end of the spectrochemical series, have Δ_o values between $30,000 \text{ cm}^{-1}$ and $50,000 \text{ cm}^{-1}$. At the other end of the series, octahedral complexes containing Br^- and I^- have relatively small Δ_o values, in many cases less than $20,000 \text{ cm}^{-1}$.

We already have discussed the important types of metal-ligand bonding in transition-metal complexes. The manner in which each type affects the value of Δ_o is illustrated in Figure 5-12. We see that a strong ($\text{L} \rightarrow \text{M}$) σ interaction increases the energy of the e_g orbitals, thereby increasing the value of Δ_o . A strong ($\text{L} \rightarrow \text{M}$) π interaction destabilizes t_{2g} , thereby decreasing the value of Δ_o . A strong ($\text{M} \rightarrow \text{L}$) π^* interaction lowers the energy of t_{2g} , thereby increasing the value of Δ_o . The spectrochemical series correlates reasonably well with the relative π -donor and π -acceptor abilities of the ligands. The π -acceptor ligands [those capable of strong ($\text{M} \rightarrow \text{L}$) π^* bonding] cause large

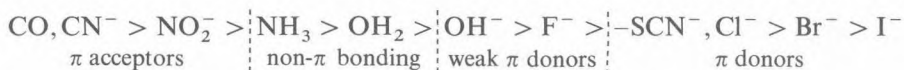


5-12

The effect on the value of Δ_o of interaction of the ligand σ , π , and π^* orbitals with the metal d orbitals.

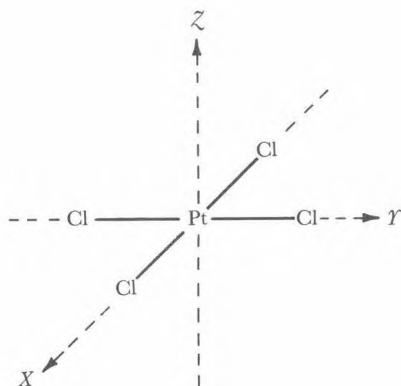
splittings, whereas the π -donor ligands [those capable of strong $(L \rightarrow M)$ π donation] cause small splittings. The ligands with intermediate Δ_o values have little or no π -bonding capabilities.

The correlation of the spectrochemical series with the π -donor and π -acceptor characteristics of several important ligands is summarized as follows:



Ionic charge of the central metal ion. In complexes containing ligands that are neither strong π donors nor π acceptors, Δ_o increases with increasing ionic charge on the central metal ion. An example is the increase in Δ_o from $V(H_2O)_6^{2+}$, with $\Delta_o = 12,400 \text{ cm}^{-1}$, to $V(H_2O)_6^{3+}$, with $\Delta_o = 17,850 \text{ cm}^{-1}$. The larger Δ_o of $V(H_2O)_6^{3+}$ probably is due to a substantial increase in σ bonding of the H_2O ligands to the more positive V^{3+} central metal ion. The enhanced σ interaction results in an increase in the difference in energy between e_g and t_{2g} .

In octahedral complexes containing strong π -acceptor ligands, an increase in oxidation number of the metal ion does not seem to be accompanied by a substantial increase in Δ_o . For example, both $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ have Δ_o values of approximately $34,000 \text{ cm}^{-1}$. When the charge on the central metal ion is increased from +2 in $Fe(CN)_6^{4-}$ to +3 in $Fe(CN)_6^{3-}$, the t_{2g} level apparently is destabilized through a decrease in π back bonding equally as much as the energy of the e_g level is raised by the greater $(L \rightarrow M)$ σ bonding.



5-13

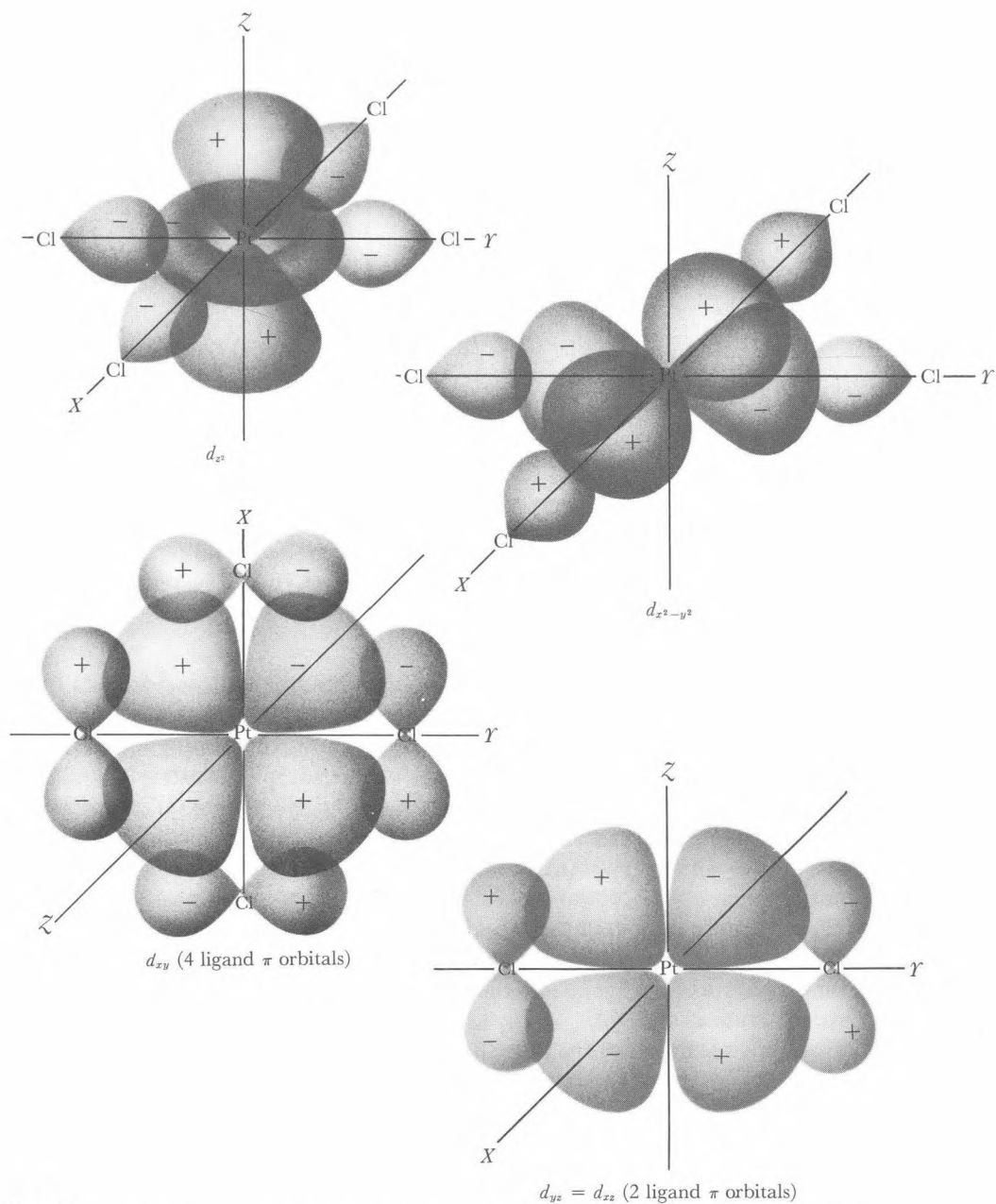
Coordinate system for a description of bonding in PtCl_4^{2-} .

Principal quantum number of the d valence orbitals. For changes from $3d$ to $4d$ to $5d$ valence orbitals of the central metal ion in an analogous series of complexes, the value of Δ_o increases markedly. For example, the Δ_o values for $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Rh}(\text{NH}_3)_6^{3+}$, and $\text{Ir}(\text{NH}_3)_6^{3+}$ are $22,900\text{ cm}^{-1}$, $34,100\text{ cm}^{-1}$, and $40,000\text{ cm}^{-1}$, respectively. Presumably the $4d$ and $5d$ valence orbitals of the ion are more suitable for σ bonding with the ligands than are the $3d$ orbitals, but the reason for this is not well understood. An important consequence of the much larger Δ_o values of $4d$ and $5d$ central metal ions is that *all* second- and third-row metal complexes have low-spin ground states, even complexes such as RhBr_6^{3-} , which contain ligands at the weak-field end of the spectrochemical series.

5-3 LIGAND FIELD THEORY FOR SQUARE PLANAR COMPLEXES

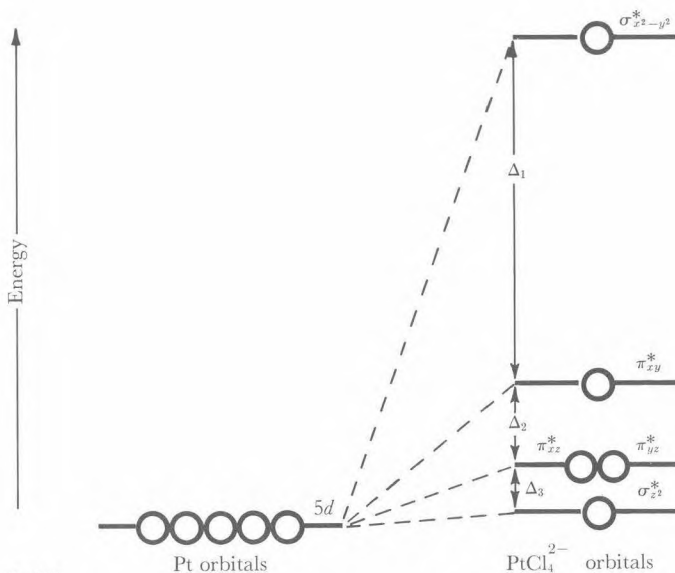
As we mentioned previously, many d^8 central metal ions form square planar complexes. The example we will use here is PtCl_4^{2-} , pictured in a reference coordinate system in Figure 5-13. The principal σ bonding involves the overlap of $3p(\sigma)$ Cl^- orbitals with the $5d_{x^2-y^2}$, $6s$, $6p_x$, and $6p_y$ metal valence orbitals. In the language of localized molecular orbital theory, the σ bonding is summarized as dsp^2 in a square planar complex.

Of principal interest here is the ligand-field splitting of the antibonding molecular orbitals derived from the metal d valence orbitals in a square planar complex. Examination of the overlaps of the Cl^- $3p$ orbitals with the Pt^{2+} $5d$ valence orbitals in PtCl_4^{2-} (Figure 5-14) reveals that only one d orbital is involved in strong σ bonding in a square planar complex, namely the $d_{x^2-y^2}$ orbital. The d_{z^2} orbital interacts weakly with the four ligand σ valence orbitals because most of the d_{z^2} orbital is directed along the Z axis away from the ligands. The metal d_{xz} , d_{yz} , and d_{xy} valence orbitals are involved in π molecular orbitals



5-14

Overlap of the metal d valence orbitals with the Cl^- ligand valence ($3p$) orbitals in a square planar complex.



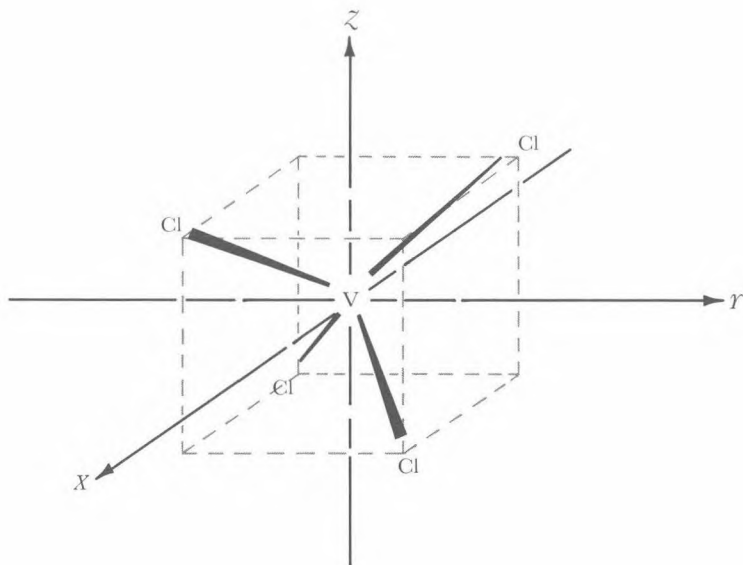
5-15

Ligand-field splitting diagram for the square planar complex PtCl_4^{2-} . For certain other square planar complexes, the $\sigma_{z^2}^*$ level may lie above π_{xz}^* , π_{yz}^* in energy.

with the ligands. The d_{xy} orbital interacts with $3p(\pi)$ valence orbitals on all four ligands, whereas each of the equivalent d_{xz} and d_{yz} orbitals interacts with only two ligands.

The ligand-field splitting in a square planar complex is rather complicated because there are four different energy levels. The ligand-field splitting diagram, which has been worked out from spectral studies of PtCl_4^{2-} , is shown in Figure 5-15. For all square planar complexes it is reasonable to place the strongly antibonding $\sigma_{x^2-y^2}^*$ orbital highest in energy. We also can position π_{xy}^* above π_{xz}^* (π_{yz}^*), since d_{xy} interacts with all four ligands. The position of the weakly antibonding $\sigma_{z^2}^*$ level probably varies in square planar complexes, depending on the nature of the ligand and the metal. As we have indicated in Figure 5-15, recent studies of PtCl_4^{2-} allow us to position $\sigma_{z^2}^*$ below the $\pi_{xz}^*-\pi_{yz}^*$ level. However, regardless of the placement of $\sigma_{z^2}^*$, the most important characteristic of the ligand-field splitting in a square planar complex is that $\sigma_{x^2-y^2}^*$ is of much higher energy than the other four orbitals, which are about the same energy.

The valence electronic configuration of the Pt^{2+} ion is $5d^8$. Because the Δ_1 splitting for PtCl_4^{2-} (Figure 5-15) is much larger than the energy required to pair two electrons in this complex, the ground-state electronic structure is $(\sigma_{z^2}^*)^2(\pi_{xz,yz}^*)^4(\pi_{xy}^*)^2$. In agreement with the ligand-field model, experimental studies show that PtCl_4^{2-} is diamagnetic.

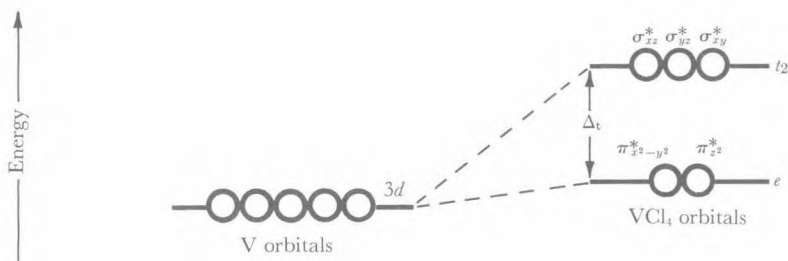
**5-16**

Coordinate system for tetrahedral VCl_4 .

We conclude from the ligand-field splitting (Figure 5-15) that a particularly favorable ground-state electronic structure for square planar complexes is the low-spin configuration $(\sigma_{z^2}^*)^2(\pi_{xz,yz}^*)^4(\pi_{xy}^*)^2$. The four relatively stable orbitals are occupied completely in this arrangement, and the high-energy $\sigma_{x^2-y^2}^*$ orbital is left vacant. Therefore the ligand-field model is consistent with the fact that complexes of the d^8 metal ions, particularly Ni^{2+} , Pd^{2+} , Pt^{2+} , and Au^{3+} , commonly exhibit square planar geometry. All d^8 square planar complexes are known to have low-spin ground-state configurations.

5-4 LIGAND FIELD THEORY FOR TETRAHEDRAL COMPLEXES

An example of a tetrahedral metal complex is VCl_4 , which is shown in a convenient coordinate system in Figure 5-16. We discussed the role of s and p valence orbitals in a tetrahedral molecule in Chapter 4. The $4s$ and $4p$ atomic orbitals of vanadium can be used to form σ molecular orbitals. Although the overlap patterns are rather complicated, the $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$ valence orbitals also are situated properly to form σ molecular orbitals. In terms of localized molecular orbitals both sd^3 and sp^3 hybrid orbitals are tetrahedrally oriented. The $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals of the central atom interact very weakly with the ligands to form π molecular orbitals.



5-17

Ligand-field splitting in a tetrahedral complex. The antibonding orbitals are divided into two sets: (1) three $\sigma^*(d)$ orbitals—the t_2 set; and (2) two $\pi^*(d)$ orbitals—the e set.

The ligand-field splitting diagram for a tetrahedral complex such as VCl_4 is shown in Figure 5-17. The antibonding molecular orbitals derived from the $3d$ valence orbitals are divided into two sets. The orbitals formed from the $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$ orbitals are of higher energy than those formed from the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals. Thus the change from octahedral to tetrahedral geometry exactly reverses the role and the energies of the d valence orbitals of the central metal ion. In a tetrahedral complex we call the three $\sigma^*(d)$ orbitals the t_2 set, and the two $\pi^*(d)$ orbitals the e set. We designate the difference in energy between t_2 and e in a tetrahedral complex as Δ_t .

With one valence electron from V^{4+} ($3d^1$), the ground-state structure of VCl_4 is $(e)^1$. The paramagnetism of VCl_4 is consistent with this configuration, which has one unpaired electron. Energy in the near-infrared region excites the electron in e to t_2 , with maximum absorption at 9010 cm^{-1} . Thus for VCl_4 , Δ_t is 9010 cm^{-1} . The molar extinction coefficient, ϵ , of the $e \rightarrow t_2$ band is 130, which is larger than a typical value for an octahedral complex, as was discussed previously.

Table 5-5. Values of Δ_t for representative tetrahedral complexes

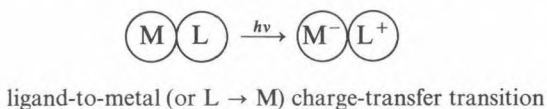
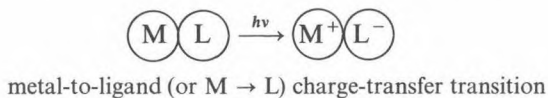
| Tetrahedral complexes | Δ_t, cm^{-1} |
|--------------------------------|----------------------------|
| VCl_4 | 9010 |
| CoCl_4^{2-} | 3300 |
| CoBr_4^{2-} | 2900 |
| CoI_4^{2-} | 2700 |
| $\text{Co}(\text{NCS})_4^{2-}$ | 4700 |

Values of Δ_t for several representative tetrahedral complexes are given in Table 5-5. Tetrahedral ligand-field splitting (Δ_t) is much smaller than octahedral splitting (Δ_o) for a given metal ion and ligand, and the relationship $\Delta_t \cong 0.45\Delta_o$ has been established from both theoretical and experimental studies. From ligand field theory we predict that the t_2 orbitals in a tetrahedral complex will not form as strong σ bonds with ligand σ orbitals as will the e_g octahedral orbitals, thereby resulting in a much less energetic t_2 level and a relatively small Δ_t value. Because of the small Δ_t values, *all* tetrahedral transition-metal complexes have high-spin ground-state configurations.

Of the dipositive metal ions, Co^{2+} (d^7) is exceptionally stable in tetrahedral complexes. Examples are CoCl_4^{2-} , $\text{Co}(\text{NCS})_4^{2-}$, and $\text{Co}(\text{OH})_4^{2-}$. The relative stability of tetrahedral Co^{2+} complexes is consistent with the fact that the $(e)^4(t_2)^3$ configuration makes maximum use of the lower-energy e level and therefore has a favorable LFSE.

5-5 CHARGE-TRANSFER ABSORPTION BANDS

For many complexes absorption bands are observed that occur in different positions from those associated with $d-d$ transitions of the central metal ion. These bands usually are in the ultraviolet region, but sometimes they occur in the visible portion of the spectrum. The bands often are quite intense because they generally involve fully allowed transitions. The types of electronic excitation that result in these strong absorptions are illustrated schematically:



Absorptions due to $\text{M} \rightarrow \text{L}$ or $\text{L} \rightarrow \text{M}$ excitation are called *charge-transfer bands*, because the transition involved requires the transfer of electronic charge to either the ligand ($\text{M} \rightarrow \text{L}$) or the metal ($\text{L} \rightarrow \text{M}$). The energies of charge-transfer bands are related closely to the oxidizing (or reducing) abilities of the metal and the ligands. The powerful oxidizing agent MnO_4^- exhibits strong $\text{L} \rightarrow \text{M}$ ($\text{O}^{2-} \rightarrow \text{Mn}^{7+}$) charge-transfer absorption in the visible region ($\bar{\nu}_{\text{max}} = 18,000 \text{ cm}^{-1}$), thereby giving the permanganate ion its intense purple color. The related chromate ion, CrO_4^{2-} , is yellow because its lowest-energy $\text{L} \rightarrow \text{M}$ ($\text{O}^{2-} \rightarrow \text{Cr}^{6+}$) band is shifted to a higher wave number ($\bar{\nu}_{\text{max}} = 26,000 \text{ cm}^{-1}$).

In both MnO_4^- and CrO_4^{2-} the lowest-energy $L \rightarrow M$ charge-transfer band is believed to be due to the excitation of a nonbonding $2p$ oxygen electron to the unoccupied e ligand-field level of the d^0 tetrahedral complex.

Charge transfer of the $M \rightarrow L$ type occurs at relatively low energy if the central metal atom or ion has reducing properties, and if the attached ligands have unoccupied orbitals of low enough energy to accept the electron. As one example, the complex $\text{Cr}(\text{CO})_6$, which contains $\text{Cr}(0)$ and the strong π -acceptor ligand CO , absorbs strongly in the ultraviolet region, with $\bar{\nu}_{\text{max}} = 35,000 \text{ cm}^{-1}$. The absorption has been attributed to electron excitation from the filled t_{2g} level of $\text{Cr}(0)$ to the unoccupied π^* level of CO .

5-6 EFFECT OF THE NATURE OF THE METAL AND THE LIGAND ON THE STABILITIES OF COMPLEXES

The reaction between a ligand and a metal ion often is classified as a *Lewis acid-base interaction*, in which the ligand (base) donates an electron pair to the metal ion (acid). Two general classes of central metal ions have been designated, according to their ability to attach various ligands. Class a comprises metal ions that form complexes with ligands in the following order of decreasing stability. Ligands containing the donor atoms N, O, and F form more stable complexes than those containing P, S, and Cl, which are more stable than those containing As, Se, and Br. These in turn are stronger than those containing Sb, Te, and I. Conversely, Class b metal ions form stronger complexes with ligands containing heavier donor atoms than with those containing N, O, and F. For instance, Al^{3+} and Fe^{3+} are Class a ions that form much more stable complexes with F^- and OH^- than with Cl^- and HS^- (or S^{2-}). An example of a Class b ion is Hg^{2+} , which forms the very weak complex HgF^+ and the increasingly more stable complexes HgCl_4^{2-} , HgBr_4^{2-} , and HgI_4^{2-} . Class b ions also tend to complex more strongly with NH_3 than with H_2O , and more strongly with H_2O than with HF . Thus Ag^+ forms $\text{Ag}(\text{NH}_3)_2^+$ in aqueous NH_3 solution.

Class a metal ions generally are nonpolarizable and combine most effectively with small, "hard" (or nonpolarizable) ligands. In contrast, Class b ions are polarizable and combine with large, "soft" (or polarizable) ligands. R. G. Pearson, of Northwestern University, has suggested the designations "hard" and "soft" for Class a and Class b acids and bases, respectively. The general rule is that soft acids combine most effectively with soft bases and hard acids combine most effectively with hard bases.

Ions with the electronic structures $4d^{10}5s^2$ or $5d^{10}6s^2$ are intermediate in behavior. When one ligand is bonded to the metal ion it acts like a Class a ion, but when four to six ligands are bonded it acts like a Class b ion. Thus PbF^+ is more stable than PbCl^+ , but PbCl_4^{2-} forms in concentrated HCl , whereas

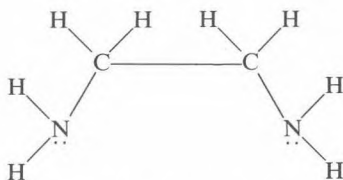
Table 5-6. Classification of positive ions (acids) as complex formers

| Class a (hard) | Intermediate | Class b (soft) |
|------------------|------------------|------------------|
| Be^{2+} | Tl^+ | Cu^{2+} |
| B^{3+} | Pb^{2+} | Ag^+ |
| Mg^{2+} | Bi^{3+} | Pt^{2+} |
| Al^{3+} | Sn^{2+} | Pt^{4+} |
| Ti^{4+} | Sb^{3+} | Pd^{2+} |
| Fe^{3+} | | Pd^{4+} |
| Mn^{2+} | | Ir^{3+} |
| Zn^{2+} | | Rh^{3+} |
| Ga^{3+} | | Hg^{2+} |
| Si^{4+} | | |

PbF_4^{2-} is not known to exist in aqueous solution. Most Class a ions have high positive charges, small radii, and closed-shell (Al^{3+}) or half-filled d shell (Mn^{2+} , Fe^{3+}) configurations. Most Class b ions have low positive charges, large radii, and nonclosed-shell configurations. Most Class b elements are found at or near the right side of each transition series. Table 5-6 classifies some common metal ions as Class a, Class b, or intermediate

Chelation and stability

Ligands that have two or more donor atoms that are situated so they can bond to the central metal ion often form unusually stable complexes. An example is the organic compound ethylenediamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, which has two nitrogen atoms with ammonialike structures, each of which is about as basic as ammonia:



ethylenediamine (en)

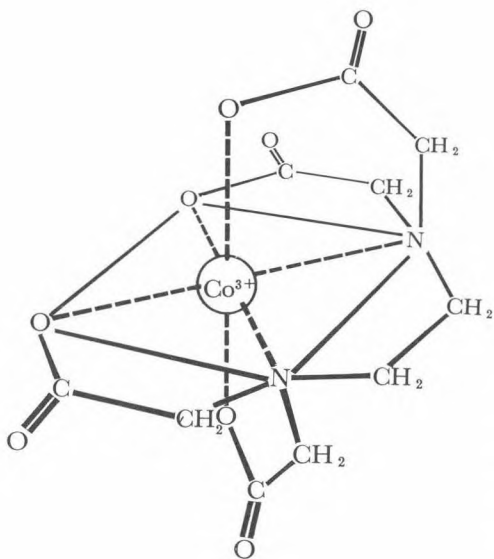
Therefore we might expect one ethylenediamine molecule to be equivalent to two ammonia molecules in complexing ability. However, the equilibrium constants for complex formation (K_f values) in Table 5-7 show that ethylenediamine is bonded much more strongly to Ni^{2+} in aqueous solution than are two ammonia molecules.

Complexes with ligands that contain more than one point of attachment are called *chelates*, from the Greek word for crab's claw. Ligands with two

Table 5-7. Standard free energies (ΔG° values) for the formation of Ni^{2+} complexes with NH_3 and $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (en) from $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ at 298°K

| Complex | $-\Delta G^\circ$, kcal | K_f |
|---|-----------------------------|----------------------|
| $\text{Ni}(\text{NH}_3)_2(\text{H}_2\text{O})_4^{2+}$ | 6.6 | 1.1×10^5 |
| $\text{Ni}(\text{en})(\text{H}_2\text{O})_4^{2+}$ | 10.6 | 4.5×10^7 |
| $\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{2+}$ | 10.3 | 1.0×10^8 |
| $\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2^{2+}$ | 19.5 | 1×10^{14} |
| $\text{Ni}(\text{NH}_3)_6^{2+}$ | 11.0 | 5.5×10^8 |
| $\text{Ni}(\text{en})_3^{2+}$ | 25.7 | 4.0×10^{18} |

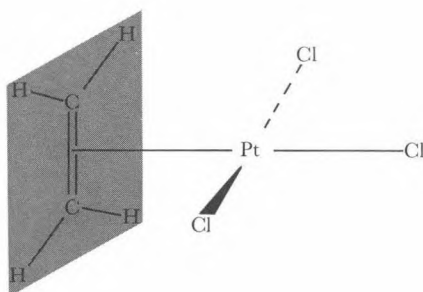
points of attachment are called *bidentates*, those with three points are called *tridentates*, and so on. The enhanced stability of chelates, as illustrated by the comparison of $\text{Ni}(\text{en})_3^{2+}$ and $\text{Ni}(\text{NH}_3)_6^{2+}$, often is called the *chelate effect*. Recent research has led to the discovery of a wide variety of polydentate ligands that wrap around central metal ions, thereby forming extremely stable complexes because of the chelate effect. A chelate containing the important hexadentate ligand EDTA (ethylenediaminetetraacetate) is shown in Figure 5-18.



5-18

The hexadentate chelating agent ethylenediaminetetraacetate (EDTA) can occupy all six octahedral coordination positions. The Co^{3+} chelate shown is a uninegative ion and usually is abbreviated $\text{Co}(\text{EDTA})^-$. EDTA is such a strong chelating agent that it will remove metals from enzymes and will inhibit their catalytic activity completely.

5-19

Structure of $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$.

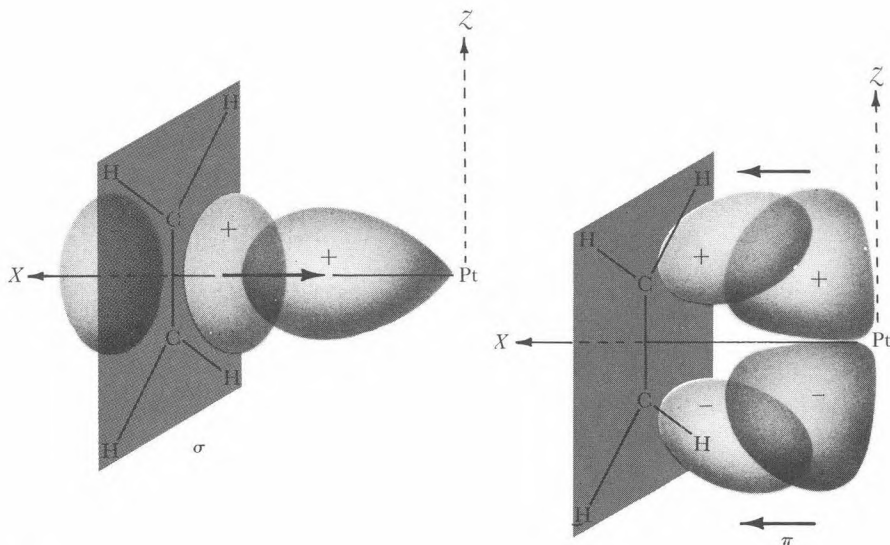
5-7 ORGANOMETALLIC π COMPLEXES OF TRANSITION METALS

Molecules that contain centrally located transition-metal atoms and organic groups attached through delocalized π -orbital networks are called *organometallic π complexes*. The first complexes of this type were discovered by the Danish chemist W. C. Zeise in 1827. The most famous complex is $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$, in which the organic molecule ethylene (C_2H_4) is bound to Pt^{2+} . More than one hundred years after its discovery, the structure of Zeise's salt was determined by x-ray diffraction methods. The structure of the $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$ ion is shown in Figure 5-19. The complex can be thought of as having a square planar structure (common to Pt^{2+}) with the ethylene bonded at one corner of the square.

The bonding between C_2H_4 and Pt^{2+} is described conveniently by the model shown in Figure 5-20. The π molecular orbitals of C_2H_4 are used to bond the molecule to the central metal ion. The filled π^b molecular orbital of C_2H_4 is used to form a σ -donor bond with an available Pt^{2+} σ orbital (a combination of the $d_{x^2-y^2}$, s , and p_x orbitals in the model shown). In addition, there is the possibility of forming a π bond between the filled metal d_{xz} orbital and the empty π^* orbital of C_2H_4 . This π back bond prevents accumulation of electron density on the metal.

Recent interest in metal π complexes can be traced to 1948, when S. A. Miller and his colleagues at the British Oxygen Company discovered that the organic compound cyclopentadiene (Figure 5-21) reacted with an iron-containing catalyst. The product of this reaction was a stable, orange, crystalline substance. This work was not published until 1951, when T. J. Kealy and P. L. Pauson accidentally made the same material by another method. The orange substance has the formula $(\text{C}_5\text{H}_5)_2\text{Fe}$ and is called *ferrocene*.

The structure of ferrocene is like a sandwich in which the meat is the central iron atom and the two bread slices are the cyclopentadienyl groups, as



5-20

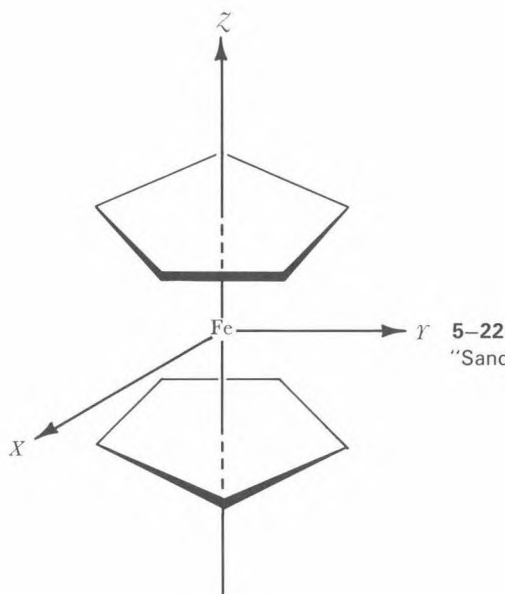
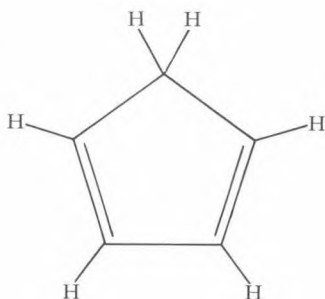
The π molecular orbitals of C_2H_4 are used to bond the molecule to Pt^{2+} in $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$.

shown in Figure 5-22. We can consider the complex as containing the d^6 central ion Fe^{2+} and two coordinated cyclopentadienyl anions (C_5H_5^-). The bonding in ferrocene commonly is described in terms of a molecular-orbital model, starting with the delocalized π molecular orbitals of the C_5H_5^- groups. Using the coordinate system shown in Figure 5-22, the d_{xz} and d_{yz} orbitals of Fe^{2+} are situated for strong bonding with the π orbitals of the C_5H_5^- groups. In addition to the d_{xz} and d_{yz} orbitals the s , p_x , p_y , and p_z iron valence orbitals presumably can be used in strong bonding with the C_5H_5^- groups. (The other d orbitals, d_{z^2} , $d_{x^2-y^2}$, and d_{xy} , play a much smaller role in the bonding.) Thus there are six bonding orbitals, which can accommodate twelve electrons. Each C_5H_5^- group furnishes six π electrons, therefore the bonding orbitals are filled in ferrocene.

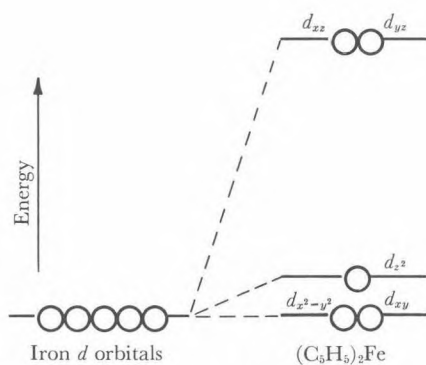
Recent research has established that the ligand-field splitting in ferrocene is that shown in Figure 5-23. The six electrons furnished by Fe^{2+} (d^6) are accommodated in the relatively low-energy d orbitals, thereby giving the ground-state configuration $(d_{x^2-y^2}, d_{xy})^4(d_{z^2})^2$. Ferrocene is diamagnetic, which agrees with this model.

The complete analysis of the ferrocene complex is as follows. Six electrons are furnished by the iron ion and are accommodated in relatively stable d orbitals. Twelve electrons are furnished by two cyclopentadienyl ions and are accommodated in six stable bonding orbitals, which are constructed from

5-21

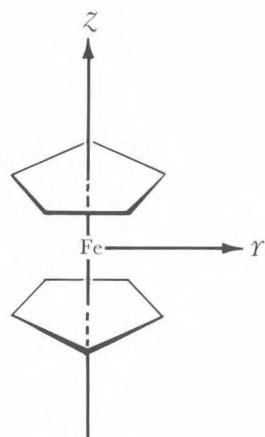
Structural formula of cyclopentadiene, C_5H_6 .

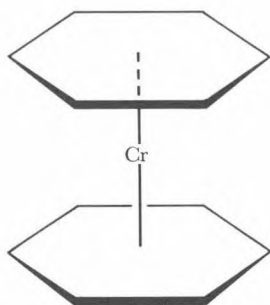
5-22
"Sandwich" structure of ferrocene, $(C_5H_5)_2Fe$.



5-23

Ligand-field splitting diagram for ferrocene.





5-24

Structure of dibenzenechromium, $(\text{C}_6\text{H}_6)_2\text{Cr}$.

the $3d_{xz}$, $3d_{yz}$, $4s$, $4p_x$, $4p_y$, and $4p_z$ Fe^{2+} orbitals and the occupied π molecular orbitals of the C_5H_5^- ions. Using this type of theoretical analysis several chemists reasoned (correctly) that many other sandwich complexes, in which the ligands furnish a total of twelve electrons and the metal atom furnishes six electrons, would be stable. The existence of a stable complex containing two molecules of benzene (six π electrons each) and a central chromium atom [$\text{Cr}(0)$; six metal valence electrons] is one noteworthy example. This sandwich complex is called *dibenzenechromium* and has the formula $(\text{C}_6\text{H}_6)_2\text{Cr}$. A schematic drawing of the structure of dibenzenechromium is shown in Figure 5-24.

Zeise's anion, ferrocene, and dibenzenechromium are only three examples of organometallic π complexes. In the past twenty years many thousands of such complexes have been prepared and studied, and organometallic chemistry is now a major area of contemporary research. Accounts of the structures and reactions of organometallic complexes may be found in most inorganic chemistry texts (see Suggestions for Further Reading).

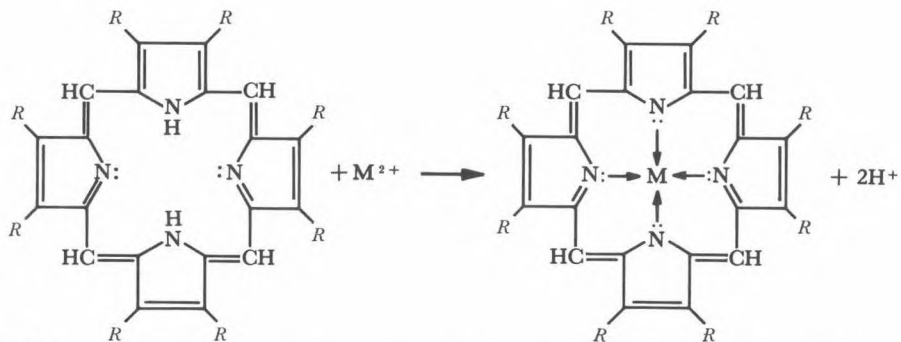
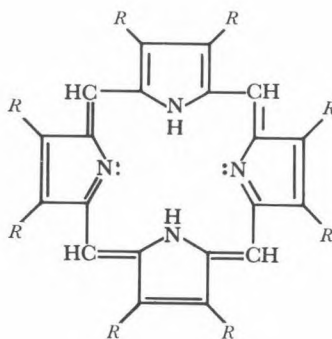
5-8 TRANSITION-METAL COMPLEXES AND LIVING SYSTEMS

Among the important transition-metal complexes in living systems are those that contain the porphyrin heterocyclic ring (Figure 5-25). Although porphyrin itself does not exist in nature, derivatives of it include the important natural products hemoglobin, chlorophyll, and cytochromes. Petroleum also contains porphyrins, which suggests that petroleum was derived from primordial living organisms.

The porphyrins are flat molecules that can act as tetradentate chelating groups (bonding through N atoms) with ions such as Mg^{2+} , Fe^{2+} , Fe^{3+} , Zn^{2+} , and Ni^{2+} in square planar complexes, as shown in Figure 5-26. The iron (as Fe^{2+} or Fe^{3+}) complex with the organic side chains shown in Figure 5-27 is called *heme*. The Mg^{2+} complex of porphyrin, with the side chains shown in Figure 5-28, is *chlorophyll*.

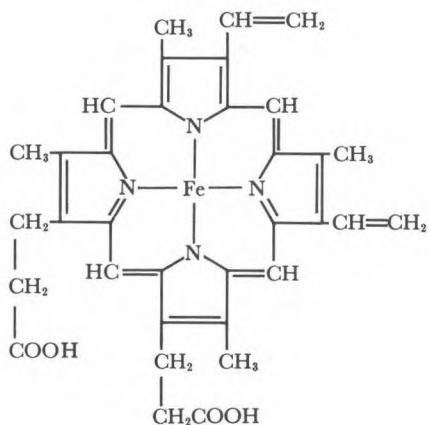
5-25

The porphyrin ring. Different porphyrins have different R groups bonded to the eight outermost positions of the ring.



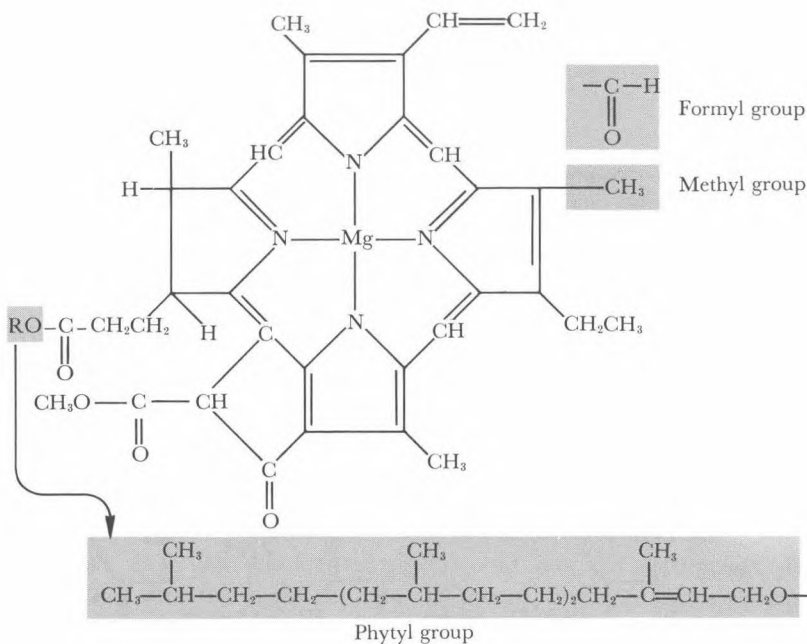
5-26

A porphyrin molecule can act as a tetradentate chelating group for metal ions such as Mg^{2+} , Fe^{2+} , Zn^{2+} , and Cu^{2+} .



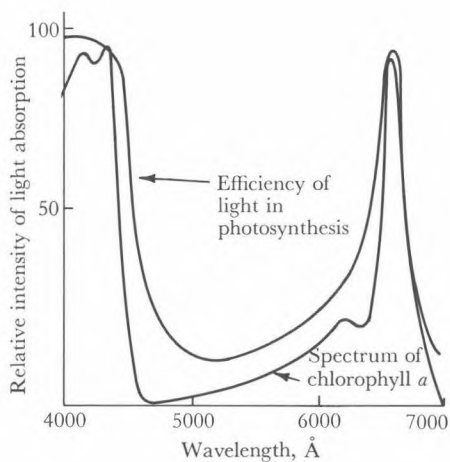
5-27

The iron porphyrin complex with the side chains as shown here is called a heme group.



5-28

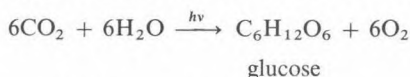
The Mg^{2+} porphyrin derivative is called chlorophyll, and is the essential molecule in photosynthesis. Chlorophyll *a* is shown here; chlorophyll *b* has a formyl group in place of the methyl group.



5-29

Chlorophyll *a* absorbs visible light except in the region around 5000 Å (green light), and thus appears green.

These two compounds, heme and chlorophyll, are the key components in the elaborate mechanism by which solar energy is trapped and converted for use by living organisms. We already have explained visible-light absorption of transition-metal complexes in terms of their closely spaced d levels. The porphyrin ring around the Mg^{2+} ion in chlorophyll also has closely spaced electronic energy levels, because the molecule contains an extensive network of conjugated double bonds. Chlorophyll molecules in plants can be electronically excited by absorbing photons of visible light (Figure 5-29). Thus chlorophyll is able to trap light and to use its energy to initiate a chain of chemical syntheses that ultimately produces sugars from carbon dioxide and water:



Scientists now believe that life evolved on earth in the presence of a reducing atmosphere, an atmosphere with ammonia, methane, water, and carbon dioxide, but no free oxygen. Free oxygen would degrade organic compounds faster than they could be synthesized by natural processes (electrical discharge, ultraviolet radiation, heat, or natural radioactivity). In the absence of free oxygen, organic compounds would accumulate in the oceans for eons until finally a localized bit of a chemical accumulated, which we would call "living."

Once developed, living organisms would exist by degrading naturally occurring organic compounds for their energy. The amount of life on earth would be limited severely if this degradation were the only source of energy. However, around three billion years ago the right combination of metal and porphyrin occurred and an entirely new source of energy was tapped—the sun. The first step that lifted life on earth above the role of a scavenger of high-energy organic compounds was an application of coordination chemistry.

Unfortunately, *photosynthesis* (as the chlorophyll photon-trapping process is called) liberates a dangerous by-product, oxygen. Oxygen was not only useless to these early organisms, it competed with them by oxidizing the naturally occurring organic compounds before they could be oxidized within the metabolism of the organisms. Oxygen was a far more efficient scavenger of high-energy compounds than living matter was. Even worse, the ozone (O_3) screen that slowly developed in the upper atmosphere cut off the supply of ultraviolet radiation from the sun and made the natural synthesis of more organic compounds even slower. From all contemporary points of view the appearance of free oxygen in the atmosphere was a disaster.

As so often happens, life bypassed the obstacle and turned a disaster into an advantage. The waste products of the original simple organisms had been compounds such as lactic acid and ethanol, which can release large amounts of energy if oxidized completely to CO_2 and H_2O . Living organisms evolved that were able to convert the poisonous O_2 to H_2O and CO_2 , and to gain the

energy of combustion of what were once its waste products. Thus aerobic metabolism had evolved.

Again, the significant development was an advance in coordination chemistry. The central components in the new terminal oxidation chain, by which the combustion of organic molecules was brought to completion, are the *cytochromes*. These are molecules in which an iron ion is complexed with a porphyrin to make a heme (Figure 5-27), and the heme is surrounded with protein. The iron changes from Fe^{2+} to Fe^{3+} and back again as electrons are transferred from one component in the chain to another. The entire terminal oxidation chain is a carefully interlocked set of oxidation-reduction reactions, in which the overall result is the reverse of the photosynthetic process:



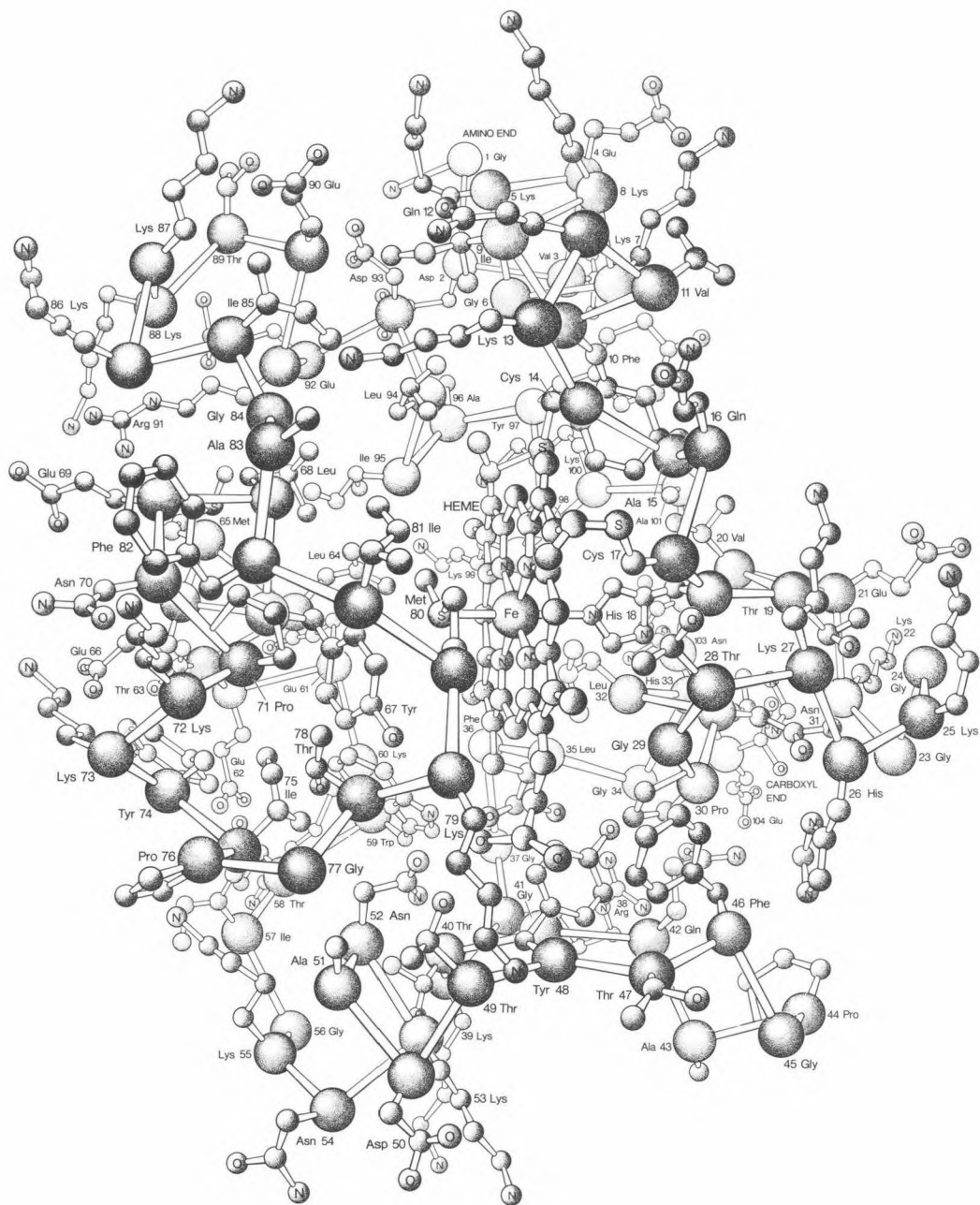
The energy liberated is stored in the organism for use as needed. The entire chlorophyll-cytochrome system can be regarded as a mechanism for converting the energy of solar photons into stored chemical energy in the muscles of living creatures.

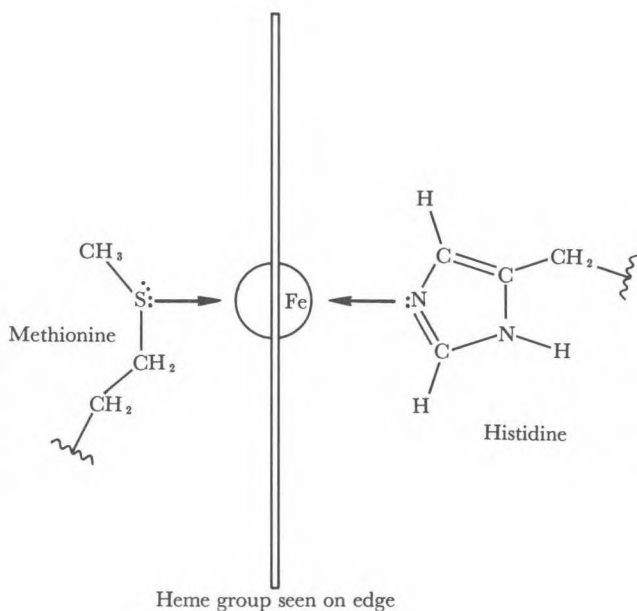
Iron atoms usually exhibit octahedral coordination. What occupies the two coordination positions above and below the plane of the porphyrin ring? In cytochrome *c*, the heme group sits in a crevice in the surface of the protein molecule (Figure 5-30). From each wall of this crevice one additional ligand extends toward the heme: on one side a nitrogen lone electron pair from a histidine side chain on the protein, and on the other side a sulfur lone pair from a methionine side chain (Figure 5-31). Therefore the bonds from the iron atom are directed octahedrally to five nitrogen atoms and one sulfur atom. The ligands around the iron in the complex, and the protein wrapped around the whole structure, allow the cytochrome *c* molecule to transfer electrons efficiently in the terminal oxidation chain.

There is one more step in the story of metal-porphyrin complexes. With the guarantee of new energy sources, multicelled organisms evolved. At this point arose the problem, not of obtaining food or oxygen, but of transporting oxygen to the proper place in the organism. Simple gaseous diffusion through body fluids will work for small organisms, but not for large, multicelled creatures. Again, a natural limit was placed on evolution.

5-30►

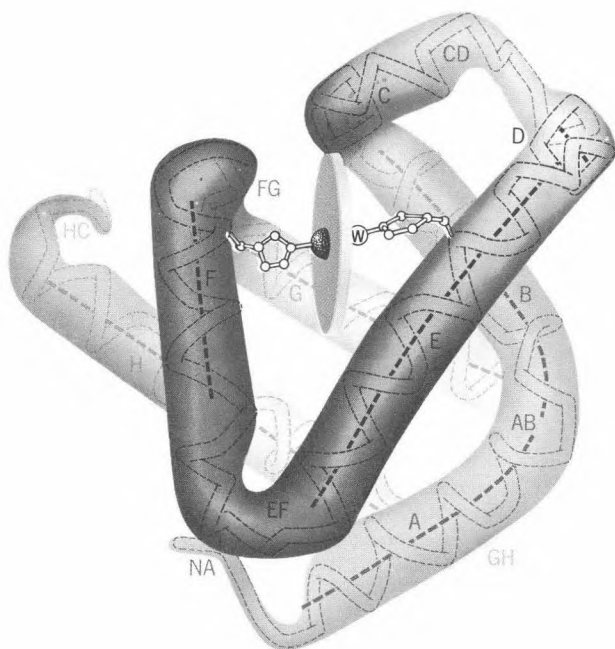
Cytochrome *c* is a globular protein with 104 amino acids in one protein chain and an iron-containing heme group. In this schematic drawing, each amino acid is represented by a numbered sphere. The heme group is seen nearly edgewise in a vertical crevice in the molecule. Copyright © 1972 Richard E. Dickerson and Irving Geis, from *Scientific American*, p. 62, April 1972.





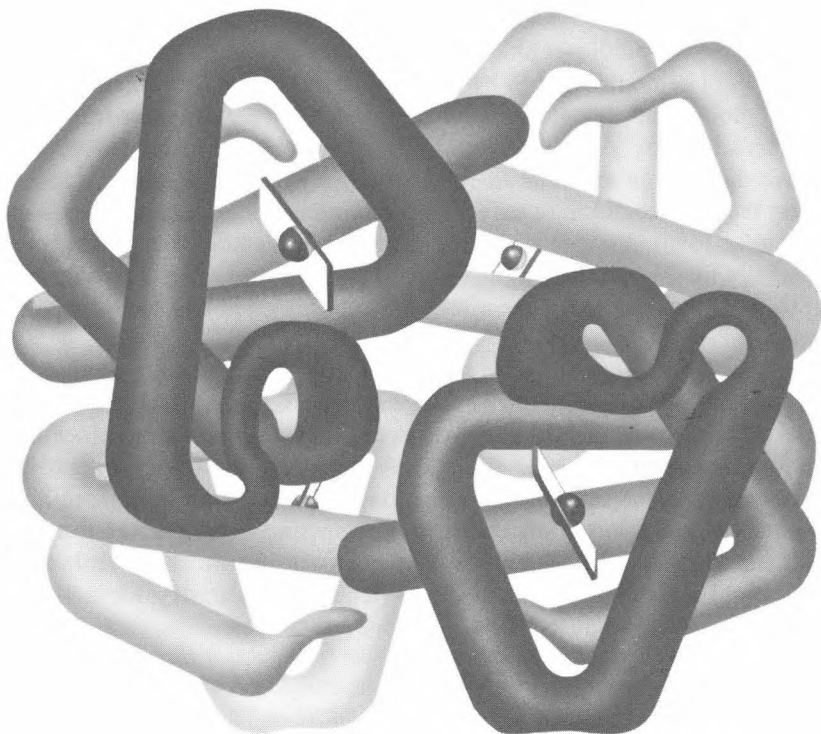
5-31

The iron atom in cytochrome *c* is octahedrally coordinated through five bonds to nitrogen atoms and one to a sulfur atom. One nitrogen atom and the sulfur atom come from side groups on the protein chain. The other four nitrogen atoms are on the porphyrin ring of the heme.



5-32

The myoglobin molecule is a storage unit for an oxygen molecule in muscle tissue. The heme group is represented by a flat disk. The iron atom is a ball at the center. The circled W marks the bonding site for O₂. The path of the polypeptide chain is shown by double dashed lines. Figures 5-32 and 5-33 copyright © 1969 by Richard E. Dickerson and Irving Geis.

**5-33**

The hemoglobin molecule is the carrier of oxygen in the bloodstream. It is built from four subunits, each of which is constructed like a myoglobin molecule. This figure and that of myoglobin are reprinted from Richard E. Dickerson and Irving Geis, *The Structure and Action of Proteins*, Harper and Row, New York, 1969.

Once again, the way out of the impasse was found with coordination chemistry. Molecules of iron, porphyrin, and protein evolved, in which Fe^{2+} could bind a molecule of oxygen without being oxidized to Fe^{3+} by it. The oxidation to Fe^{3+} was, in a sense, “aborted” after the first binding step. Oxygen merely was carried along to be released under the proper conditions of acidity and oxygen scarcity. Two compounds evolved, *hemoglobin*, which carries oxygen in the blood, and *myoglobin*, which receives and stores oxygen in the muscles until it is needed in the cytochrome process.

The myoglobin molecule is depicted in Figure 5-32. As in cytochrome *c*, four of the six octahedral iron positions are taken by heme nitrogens. The nitrogen of a histidine is bonded in the fifth position. However, the sixth position has no ligand. This is the place where the oxygen molecule bonds, marked by the circled W. In myoglobin, the iron is in the Fe^{2+} state. If the iron is oxidized to Fe^{3+} , the molecule is inactivated and a water molecule occupies the oxygen position.

Hemoglobin is a package of four myoglobinlike molecules (Figure 5-33). From x-ray crystallographic studies it has become apparent that the four subunits of hemoglobin shift by 7 Å relative to one another when oxygen bonds. Hemoglobin and myoglobin now become a model system for transition-metal chemists to study. Why does bonding at the sixth ligand site of the iron complex cause the protein subunits to rearrange? Why does the oxygen molecule fall away from hemoglobin in an acid environment (such as in oxygen-poor muscle tissue)? How is the coordination chemistry of hemoglobin and myoglobin so carefully meshed that myoglobin binds oxygen just as hemoglobin releases it at the tissues? These are questions that probably will be answered from further research.

Heme also is at the active sites in enzymes that decompose H_2O_2 to H_2O and O_2 . Manganese, cobalt, copper, and molybdenum, among others, also are essential transition metals in enzyme catalysis. With the evolution of myoglobin and hemoglobin, the size limitation was removed from living organisms. Thereafter, all of the multicelled animals that we ordinarily see around us evolved. In the sense that transition metals and double-bonded organic ring systems such as porphyrin are uniquely suited for absorbing visible light, and their combinations have a particularly rich redox chemistry, life indeed depends on coordination chemistry.

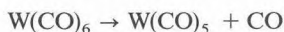
SUGGESTIONS FOR FURTHER READING

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 R. E. Dickerson, "The Structure and History of an Ancient Protein," *Scientific American* (April, 1972).
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QUESTIONS AND PROBLEMS

1. Why are octahedral complexes with d^3 and d^6 configurations particularly stable? Which electronic configurations would you predict to be more important for stability in high-spin complexes? In low-spin complexes?
2. All octahedral complexes of V^{3+} have the same number of unpaired electrons, no matter what the nature of the ligand. Why is this so?
3. How does the ligand field theory account for the order of ligands in the spectrochemical series?

4. What is a chelate? If porphyrin is a tetradentate chelating group, and ethylenediamine is a bidentate chelating group, how would triethylenetetraamine, diethylenetriamine, and ethylenediaminetetraacetate (EDTA) be described?
5. Explain why $\text{Co}(\text{CN})_6^{3-}$ is extremely stable but $\text{Co}(\text{CN})_6^{4-}$ is not.
6. Explain the fact that most complexes of Zn^{2+} are colorless.
7. Explain why octahedrally coordinated Mn^{3+} is very unstable, whereas octahedral complexes of Cr^{3+} are extremely stable.
8. Using ligand field theory predict the number of unpaired electrons in the following complexes: FeO_4^{2-} , $\text{Mn}(\text{CN})_6^{3-}$, NiCl_4^{2-} (tetrahedral), PdCl_4^{2-} (square planar), MnCl_4^{2-} , $\text{Co}(\text{en})_3^{3+}$, $\text{Co}(\text{en})_3^{3+}$, $\text{Rh}(\text{NH}_3)_6^{3+}$, CoBr_4^{2-} , and $\text{Pt}(\text{NH}_3)_4^{2+}$.
9. Carbon monoxide is a strong-field ligand that stabilizes transition metals in unusually low oxidation states. For example, $\text{V}(\text{CO})_6$ and $\text{V}(\text{CO})_6^-$ both are stable complexes. What are the ground-state electronic configurations of these two complexes in the ligand-field levels t_{2g} and e_g ? Which member of the series $\text{V}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$, and $\text{Mn}(\text{CO})_6$ would you expect to be most stable? Which would be least stable? Why?
10. One of the most toxic substances known to man is tetracarbonylnickel(0), $\text{Ni}(\text{CO})_4$. Predict its geometrical structure, using localized molecular orbital theory. Formulate the ground-state electronic structure of $\text{Ni}(\text{CO})_4$ using ligand field theory. Would you expect to observe $d-d$ transitions in this compound? Why or why not?
11. A complex widely used in studying reactions of octahedral complexes is $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$. Actually, this complex is octahedral only in an approximate sense, because NH_3 and Cl^- have different ligand-field strengths. How would you modify the ligand-field energy levels of $\text{Co}(\text{NH}_3)_6^{3+}$ in formulating a splitting diagram for $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$? (For convenience, place the Cl^- ligand along the Z axis of a Cartesian coordinate system.) Apply your theory to explain the fact that $\text{Co}(\text{NH}_3)_6^{3+}$ is yellow (absorbs light at 4300 Å), whereas $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ is purple (absorbs light at 5300 Å). Which d orbital receives the electron in the excitation giving rise to the 5300-Å band in $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$? Why?
12. If $\text{Mn}(\text{H}_2\text{O})_6^{2+}$, $\text{Fe}(\text{H}_2\text{O})_6^{2+}$, and $\text{Co}(\text{H}_2\text{O})_6^{2+}$ had been low-spin, how would Figure 5–8 have appeared?
13. Why are Ni^{2+} complexes with weak-field ligands octahedral and those with strong-field ligands square planar?
14. Electronically excited molecules often emit light just as do excited atoms. However, excited molecules also may use their excess energy to break chemical bonds and thereby undergo chemical reactions that might not occur otherwise. An example is the metal complex $\text{W}(\text{CO})_6$. The molecule is unreactive in its ground state, but upon irradiation by light of 3000-Å wavelength the following reaction occurs:



From this information estimate an upper limit, in kcal mole^{-1} , for the $\text{W}-\text{CO}$ bond energy. As the reaction proceeds the concentration of carbon monoxide increases. Is there a possibility that the secondary reaction



can occur? Why or why not?

15. a) Give the ligand-field electronic configuration of the ground state of W(CO)_6 . Is the complex diamagnetic or paramagnetic? The first electronic absorption band occurs at about $31,000\text{ cm}^{-1}$. Assign this band to an electronic transition in the complex. Is the photochemical dissociation of W(CO)_6 to $\text{W(CO)}_5 + \text{CO}$, described in Problem 14, reasonable? Explain.
 b) The W(CO)_5 molecule has a square pyramidal structure. Assume a reference coordinate system in which only one CO ligand is along the Z axis and predict the ligand-field splitting for this complex. W(CO)_5 absorbs light strongly at $25,000\text{ cm}^{-1}$. Assign the band to an electronic transition in W(CO)_5 and explain why the absorption is at lower energy than in W(CO)_6 .
16. The CuCl_2 molecule has been observed in the gas phase. It has a linear structure. Assume that the internuclear line is along the Z axis and predict the ligand-field splitting diagram for CuCl_2 . What is the ground-state electronic configuration of CuCl_2 ? How many $d-d$ transitions should be observed? What are the transition assignments?
17. Consider the following complex ions: MnO_4^{3-} , Pd(CN)_4^{2-} , NiI_4^{2-} , $\text{Ru(NH}_3)_6^{3+}$, MoCl_6^{3-} , IrCl_6^{3-} , AuCl_4^- , and FeF_6^{3-} . Use ligand field theory to predict the structure and number of unpaired electrons in each ion.
18. Give reasonable examples of the following: (a) d^5 high-spin octahedral complex; (b) low-spin square planar complex; (c) d^0 tetrahedral complex; (d) d^5 low-spin octahedral complex; (e) d^3 complex.
19. (a) Calculate the energy in cm^{-1} of the absorption spectral line in isolated Li^{2+} corresponding to the transition $1s \rightarrow 3d$. Do the $1s \rightarrow 3s$ and $1s \rightarrow 3p$ transitions have the same energy? (b) Now assume that the Li^{2+} is placed in an octahedral ligand field. How many different electronic transitions would you expect to observe from the $1s$ orbital to the $n = 3$ orbitals in this ligand field? How many would be expected in a tetrahedral field? How many in a square planar field?
20. Which complex in each of the following pairs would you expect to be more stable: (a) PtCl_4^{2-} or PtI_4^{2-} ; (b) $\text{Fe(H}_2\text{O)}_6^{3+}$ or $\text{Fe(NH}_3)_6^{3+}$; (c) FeCl_4^- or FeI_4^- ; (d) ZnCl_4^{2-} or ZnBr_4^{2-} ; (e) HgCl_4^{2-} or HgBr_4^{2-} ; (f) $\text{Ag(H}_2\text{O)}_6^+$ or $\text{Ag(NH}_3)_2^+$; (g) BF_4^- or BCl_4^- ; (h) $\text{Cu(NH}_3)_4^{2+}$ or $\text{Cu(H}_2\text{O)}_4^{2+}$.
21. Cobaltocene, $\text{Co(C}_5\text{H}_5)_2$, and nickelocene, $\text{Ni(C}_5\text{H}_5)_2$, have sandwich structures similar to that of ferrocene. Formulate the ground-state electronic structures for these two organometallic π complexes. How many unpaired electrons are there in each case? Would you expect cobaltocene to be more, or less, stable than ferrocene? Why?
22. Cobaltocene can be oxidized to the cobalticenium ion, $\text{Co(C}_5\text{H}_5)_2^+$. Would you expect this ion to be diamagnetic, or paramagnetic? Explain.
23. Predict which complex in each of the following pairs will have the lower-energy $d-d$ transition: (a) $\text{Co(NH}_3)_5\text{F}^{2+}$ or $\text{Co(NH}_3)_5\text{I}^{2+}$; (b) $\text{Co(NH}_3)_5\text{Cl}^{2+}$ or $\text{Co(NH}_3)_5\text{NO}_2^{2+}$; (c) $\text{Pt(NH}_3)_4^{2+}$ or $\text{Pd(NH}_3)_4^{2+}$; (d) Co(CN)_6^{3-} or Ir(CN)_6^{3-} ; (e) $\text{Co(CN)}_5\text{H}_2\text{O}^{2-}$ or $\text{Co(CN)}_5\text{I}^{3-}$; (f) $\text{V(H}_2\text{O)}_6^{2+}$ or $\text{Cr(H}_2\text{O)}_6^{3+}$; (g) RhCl_6^{3-} or Rh(CN)_6^{3-} ; (h) $\text{Ni(H}_2\text{O)}_6^{2+}$ or $\text{Ni(NH}_3)_6^{2+}$.

24. Predict whether a reaction will occur when Br^- is added to aqueous solutions of each of the following complex ions: FeF_6^{3-} , PdCl_4^{2-} , HgI_4^{2-} , BF_4^- , $\text{Pt}(\text{NH}_3)_3\text{I}^+$, $\text{Co}(\text{NH}_3)_5\text{I}^{2+}$, $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$, and $\text{Pt}(\text{NH}_3)_3\text{H}_2\text{O}^{2+}$.
25. Many complexes of Cu^{2+} have square planar structures. What is the ground-state electronic configuration of a square planar Cu^{2+} complex? How many $d-d$ transitions of different energies can be expected?
26. A common inorganic chemical compound, ferric ammonium sulfate, has the formula $\text{Fe}_2(\text{SO}_4)_3(\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$. Large crystals of the compound are very pale violet, due to weak absorptions (ϵ values between 0.05 and 1) in the visible region of the spectrum. The Fe^{3+} in the compound is present as the hexaquo complex ion, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. Using ligand field theory formulate an explanation of the weak absorption bands.
27. The ferrocyanide ion, $\text{Fe}(\text{CN})_6^{4-}$, does not exhibit an absorption band in the visible region, but ferricyanide, $\text{Fe}(\text{CN})_6^{3-}$, absorbs strongly at approximately $25,000\text{ cm}^{-1}$. What type of electronic transition is responsible for this strong absorption, which makes $\text{Fe}(\text{CN})_6^{3-}$ red?
28. Explain the fact that the lowest $\text{L} \rightarrow \text{M}$ charge-transfer band shifts from $18,000\text{ cm}^{-1}$ in MnO_4^- to $26,000\text{ cm}^{-1}$ in CrO_4^{2-} .
29. Would you expect a given $\text{M} \rightarrow \text{L}$ charge-transfer transition to be at lower, or higher, energy in $\text{Cr}(\text{CO})_6$ than in $\text{Mn}(\text{CO})_6^+$? Why?
30. The yellow complex HgI_4^{2-} exhibits a strong absorption band at $\bar{\nu}_{\text{max}} = 27,400\text{ cm}^{-1}$. What type of electronic transition is responsible for this band?